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Non-aqueous solv.

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(2) acids (3) bases
ammonia (5) nitrogen
monia (7) acetic acid
fluoride
dioxide
des (11) halogens
re

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NON-AQUEOUS SOLVENTS

Applications as Media
for Chemical Reactions

By L. F. AUDRIETH and BETTY ACKERSON OGG
THE CHEMISTRY OF HYDRAZINE

By L. F. AUDRIETH and JACOB KLEINBERG
NON-AQUEOUS SOLVENTS: Applications
as Media for Chemical Reactions

NON-AQUEOUS SOLVENTS

Applications as Media
for Chemical Reactions

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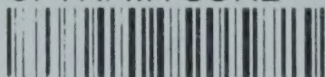
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Non-aqueous solv..

To
THE PIONEERS IN THE FIELD OF
NON-AQUEOUS SOLVENT CHEMISTRY

EDWARD CURTIS FRANKLIN

CHARLES A. KRAUS

PAUL WALDEN

PREFACE

"Much important chemistry, particularly important in the field of organic chemistry, has been obscured by our slavish devotion to water." No truer words were ever written than these, which appear in an article by James B. Conant and Norris F. Hall. The same statement could be repeated with equal emphasis in its application to the field of inorganic chemistry.

Too little is known in a general way about the properties and the potentialities of the more common non-aqueous solvents. It is true that physicochemical researches in this field are numerous. The electrochemistry of non-aqueous systems has been investigated by many, notably by Charles A. Kraus in this country and by Paul Walden in Europe. There is no question but that these studies have been of real value in extending the boundaries of theoretical chemistry. On the other hand, less effort has been made to present the "chemistry" of non-aqueous systems, that is, to show how such solvents can be used to effect various chemical reactions and syntheses.

There will always be the doubting Thomases among our professional colleagues who will ask us to justify our enthusiasm for this branch of chemistry. What can be accomplished in the fields of inorganic, organic, and analytical chemistry by employing non-aqueous media? What solvents may be employed advantageously to effect specific reactions? Obviously, these questions can be answered only by example and by precept, that is, by reviewing what has been done and by emphasizing, in so far as our present state of knowledge permits, why particular solvents do give better results than others. It is our purpose to show how non-aqueous solvents can be used as media for carrying out chemical reactions and, by so doing, to stimulate others to enter this field of research or to make practical use of recorded observations.

In line with this objective we have seen fit, first of all, to discuss the physical characteristics of solvents and to indicate briefly what special properties determine the usefulness of a solvent.

Since acids and bases are found so universally in chemical systems we have considered it advisable to review modern concepts of acidity

and basicity. We do not presume to pass judgment on the relative merits of the various proposals, for we have found in our own work that all the modern concepts dealing with acid-base relationships are useful. We would not wish to ridicule the followers of the "cult of the proton"; nor would we presume to extend the Lewis concept as far as have those ardent proponents of this theory who have merely renamed the coordination theory and now call it the electronic theory of acids and bases. We have certainly found the solvent system concept very useful in interpreting the behavior of a wide variety of solutes in protonic and non-protonic media; we recognize, however, that formal analogies can be overextended.

We have chosen for more complete discussion those solvents which we believe to possess greatest utility when employed in the laboratory. Four chapters are devoted to a discussion of liquid ammonia chemistry and to a survey of reactions which inorganic and organic chemists have effected using this medium. The solvent system concept applied to ammonia as the parent substance of the nitrogen system of compounds is used as a working hypothesis for the elucidation of reactions which take place in this medium. There is no question but that liquid ammonia has become a useful solvent, especially since techniques for handling it have been worked out thoroughly.

Less well known, but interesting as potentially useful solvents, are the various derivatives of ammonia which are taken up in Chapter 7. The amines, pyridine, hydrazine, hydroxylamine, hydrogen cyanide, acetonitrile, formamide, and acetamide, are discussed briefly, first, to illustrate how the chemical character of a solvent can be modified by dissolution therein of various classes of solutes and, second, to direct attention to these and related compounds as solvents worthy of more thorough investigation.

Three acidic solvents have been given more detailed consideration, namely, acetic acid, sulfuric acid, and hydrogen fluoride. Especially interesting are the potential uses of acetic acid in analytical chemistry, of sulfuric acid as a medium for carrying out organic reactions, and of hydrogen fluoride as a solvent in which to carry out the synthesis of a wide variety of fluorine compounds.

Sulfur dioxide is a typical aprotic solvent. It is readily available and can be handled without very much difficulty. Particularly worthwhile are the uses which sulfur dioxide should find as an extractive solvent and as a medium for halogenation, sulfonation, acylation, and alkylation reactions.

Two chapters are then devoted to a discussion of acid chlorides and

to the interhalogens as media for chemical reactions. We do not feel that we have deviated from our objective in presenting the chemistry of these solvent systems. Such compounds as phosphorus(V) oxychloride, sulfuryl chloride, and thionyl chloride are important chemical commodities. While bromine trifluoride is hardly a solvent of general utility, its investigation has led to the synthesis of quite a number of new classes of compounds. Its investigation as a solvent has therefore been justified in a practical way.

The average chemist rarely extends his experimental efforts beyond a rather narrow range of temperatures. It is significant, however, that many of our more important industrial processes in the fields of metallurgy and ceramics involve high-temperature liquid-phase reactions. Solvent relationships and the acidic or basic properties of solutes in such high-temperature fused systems have not been given the same thorough treatment that characterizes our state of knowledge with respect to solvents which are customarily employed at ordinary temperatures. It is for this reason that we have felt constrained to bring to the attention of the chemical public a few of the reactions possible in such systems and have devoted the final chapter to some interesting aspects of high-temperature chemistry. Even though this discussion may be somewhat out of context with what has preceded it, we are motivated by a certain missionary zeal in the hope that more attention will be given to solvents which are usable only at higher temperatures.

Actually, we have suffered from an embarrassment of riches in the choice of solvents which we have made the basis for discussion in this book. We realize that we may be criticized for omitting altogether any reference to the solvent properties of the alcohols, glycols, ketones, and esters and of the hydrocarbons and their halogenated derivatives. These organic solvents certainly deserve thorough treatment, and it is our hope that those more familiar than we are with solvent relationships in these substances will undertake to make available a survey covering these compounds as media for chemical reactions.

In presenting this survey of non-aqueous solvent chemistry we have been guided by considerations which would appeal more specifically to those among our professional colleagues who are particularly interested in synthetic chemistry. Our treatment is not exhaustive, but we do hope that our efforts will stimulate others to employ non-aqueous solvents and will help to dispel the feeling among chemists generally that there is something mysterious about reactions in solvents other than water.

We are particularly grateful to Professors W. Conard Fernelius, Warren C. Johnson, and George W. Watt for granting us permission to quote extensively from the very excellent review articles dealing with liquid ammonia which each has published jointly and individually in the *Journal of Chemical Education* and in *Chemical Reviews*. Many of our professorial colleagues at the University of Illinois and at the University of Kansas have been most helpful in giving freely of their special knowledge in reviewing various portions of the manuscript. Especially do we wish to express our thanks to Dean Arthur W. Davidson and to Professor Robert Taft for their help and advice. We also acknowledge the very helpful suggestions made by Professor George W. Watt, who reviewed thoroughly and completely the original manuscript. We also thank the Graduate Research Committee of the University of Kansas for financial assistance in the preparation of the manuscript.

Each of us has presented over the years a graduate course dealing with non-aqueous solvent chemistry. Our students have in this connection prepared comprehensive reviews covering various special phases of the chemistry and physical chemistry of reactions in various solvents. We are grateful to them for helping us to build up a tremendous file of information which has served in a real sense as the source material for this book. We would call particular attention to the chapter on halogens and interhalogens as solvents which is based on a seminar presentation of Mr. Niels C. Nielsen.

We also wish to take this opportunity to express our gratitude to William Channing Smith, Earle S. Scott, and Paul G. Gordon, who helped us with the manuscript. We are indebted to many others, but most of all to our wives, Maryon Trevett Audrieth and Jane Crawford Kleinberg, who have encouraged us in all our scientific efforts.

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November, 1952

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PROPERTIES OF SOLVENTS

INTRODUCTION

A tremendous amount of experimental work has been carried out during the last fifty years on the physical and chemical properties of a wide variety of non-aqueous solutions. Although much of this work has been of a fundamental nature, it is only recently that these investigations have begun to pay practical dividends. Reactions are now carried out in liquid ammonia under pressure on a fairly substantial scale. Ammonia is widely used not only for liquid phase reactions, but also for reactions at higher temperatures in the vapor phase.

Sulfur dioxide, another relatively inexpensive inorganic material, has been used as a selective and extractive solvent; it has been only within the last few years that the possible use of this very interesting solvent for organic reactions has been disclosed. Fifty years ago the suggestion that anhydrous hydrogen fluoride be employed as a solvent would have been met with incredulity. Advances in techniques for the manufacture and the handling of this material have opened up interesting technical possibilities. Fundamental consideration of hydrogen fluoride as a solvent has helped to expand tremendously the whole field of fluorine chemistry leading to the synthesis and isolation of a host of new compounds, many of which possess industrially interesting properties.

Acetic acid and sulfuric acid are solvents which have long been used by the organic chemist for numerous reactions. Acid-base relationships which obtain in glacial acetic acid are sufficiently unique to warrant its rather widespread use in analysis and for the identification of various organic compounds, especially substances which are weakly basic in nature. Although sulfuric acid has been used as a co-reactant with nitric acid to effect the nitration of organic compounds, it is only since about 1940 that the true nature of such mixed acid combinations has been generally recognized. The very important role which sulfuric acid plays as a solvent for nitric acid in facilitating ionization to give the nitronium ion, NO_2^+ , is shared by only a few

other materials. Sulfuric acid is certainly a solvent which warrants greater consideration. It is an inexpensive chemical and is produced in tremendous tonnages. Sulfuric acid does bring about some unusual changes in the properties of solutes which make possible reactions that are not achievable in any other medium.

But our thinking need not be limited only to those substances which are liquids from approximately -50° to 200°C . High-temperature fused melts and glasses are non-aqueous solvents which have been used since early times. Efforts have been made by the ceramist and by the metallurgist to study glasses and slags in order to elucidate the relationships which characterize these very complex and complicated systems. There is no question but that reactions may occur in such high-temperature fused media which are quite analogous to those occurring in aqueous and non-aqueous systems at ordinary temperatures. However, these high-temperature systems have been explored only superficially from a fundamental point of view. This statement in no way detracts from the technological accomplishments of the ceramist and the metallurgist, who have solved successfully many of the problems encountered in the handling and use of such high-temperature melts. It is suggested, however, that a more intensive fundamental study of behavior of substances in such melts is now desirable and not only may lead to an interpretation of the results which have been recorded and have been obtained on an empirical basis, but also may aid in furthering the more widespread use of systems of this type. Some effort has been made to apply generalizations which characterize aqueous and non-aqueous solutions to such an-solvous systems at higher temperatures. Notable success has been achieved, it is believed, in extending to such high-temperature media the various modern concepts which define acid-base relationships in ordinary solvents.

NON-AQUEOUS SOLVENTS BEFORE 1900. The advances in the fundamental chemistry of non-aqueous solutions during the last half century are all the more striking since the opinion was prevalent before 1900 that water was indeed the only solvent in which typical ionic and metathetical reactions could be carried out. That such a misconception should have persisted so long is all the more unusual since Faraday had come to the conclusion as early as 1834 that water is only one of many substances which might serve as ionizing media. However, in the literature before 1900 the statement is found repeatedly that water, and only water, may serve as an ionizing solvent. This was certainly the point of view held by Wilhelm Ostwald, by Armstrong, and by Kohlrausch, all of whom were very much interested

in the behavior of aqueous solutions. Although occasional efforts had been made to study in a fragmentary way the behavior of typical salts when dissolved in non-aqueous solvents, unusual observations gleaned from such experiments were considered special cases; water was considered the prototype for possible behavior of solutes in other systems. Today, however, we recognize that water is anomalous in many respects and that concepts defining the behavior of solutions can often be developed more readily on the basis of observations in non-aqueous solvents.

A summary of early observations dealing with solubilities and theoretical relationships in non-aqueous solvents is presented by Walden (1) in his very comprehensive treatise, *Elektrochemie Nichtwässriger Lösungen*. Boyle (about 1660) recognized alcohol as an unusual solvent and referred to the fact that it dissolves the chlorides of iron and copper. Lemery (1675) described "alcohol as a solvent for many things." The Dutch chemist Boerhaave (1732) stated that alcohol dissolves water, all wines, all fermented liquors, pure oils, plant resins, volatile alkalies, some fixed alkalies and soaps, whereas salt, saltpeter, and sal ammoniac do not dissolve. Alcohol was used by the Russian chemist Lowitz (1796) to separate calcium and strontium chlorides from barium chloride, which is insoluble.

According to Walden, anhydrous acetic acid was first prepared by Lowitz (1789), who observed that boric acid is soluble, but that carbonates do not dissolve or react with the solvent. Gmelin (1848) summarized the solubilities of various substances in ether. Liebig prepared acetone (1832) and commented on the fact that it resembles ethyl alcohol as a solvent; but, unlike ethyl alcohol, it does not dissolve potassium chloride or potassium hydroxide. Methyl alcohol was characterized by Dumas (1835) as a more satisfactory solvent for oxygen-rich compounds than ethyl alcohol.

It was further recognized by early workers that solvents are not necessarily inert towards dissolved solutes, but may react to form crystalline compounds resembling the hydrates. The English chemist Graham (1828) was the first to prepare compounds containing ethyl alcohol of crystallization. Dumas (1835) found that methyl alcohol forms crystalline compounds with calcium chloride and barium oxide. Liebig (1833) prepared an addition compound of ethyl acetate with calcium chloride. The crystalline compound between tin(IV) chloride and ether was first prepared by Kuhlmann in 1840. Chemical evidence was, therefore, at hand to demonstrate that quite a number of substances do resemble water in their ability to form compounds containing solvent of crystallization.

Similarities between water and non-aqueous solvents were also emphasized by the work which Raoult began in 1880 on determination of molecular weights. The original investigations were carried out in aqueous solution and were then extended to non-aqueous solvents. In most cases, observations were quite similar in that freezing point depressions and lowering of the vapor pressure were found to depend on the amount of dissolved solute.

Miscellaneous efforts were also made by a number of investigators to study the conductance of solutions of electrolytes in non-aqueous solvents, but no logical conclusions could be drawn from these data. The Italian chemist Carrara (1894) undertook the first systematic investigation of the conductance of a single electrolyte, triethylsulfonium iodide, in a number of different solvents (acetone, methyl alcohol, ethyl alcohol, and benzyl alcohol) and later studied the ionization of various acids, bases, and salts in methyl alcohol. No real beginning was made, however, until Walden and his co-workers at the turn of the century began their extensive and continuing investigations of the electrochemistry of various electrolytes in sulfur dioxide, thionyl chloride, and other presumably inert inorganic and organic solvents. Franklin and Kraus began their investigations with liquid ammonia at about the same time. It was only after these two groups had begun their experimental efforts that serious attention was directed toward non-aqueous systems. Even so, such recognition as these investigators first received was of a negative rather than of a constructive nature since a large group of non-conformists, among them Kahlenberg, were making deliberate efforts to attack the Arrhenius theory by citing its non-applicability to non-aqueous systems.

Investigations undertaken in the last fifty years, although exploratory and directional, have been essentially fundamental. Due credit must be given to the physical chemist and the electrochemist, who have carefully and thoroughly evaluated the behavior of solutions of a wide variety of substances in many different non-aqueous solvents. Among the first to take advantage of the synthetic possibilities of such non-aqueous solvents was the organic chemist. However, only liquid ammonia seemed to receive attention at first, possibly because use of this substance brought with it the further recognition that nitrogen compounds are related to ammonia as a parent substance in the same way that oxygen compounds are to be considered derivatives of water. In promulgating the "nitrogen system" concept, Franklin (2) paved the way for the organization of nitrogen chemistry and the systematic classification of the large number of nitrogen com-

pounds which had been isolated and characterized, but whose intimate relationship had not been well established. Work with non-aqueous solvents also made it necessary to modify accepted definitions of acids and bases. Since these classes of substances are found so universally in many chemical systems and play such important roles in many reactions it became necessary to develop more widely applicable concepts with respect to acid-type and base-type compounds. There is no question but that the experimental findings of Franklin and of Kraus furnished the basic information which led to the development of the protonic concept and of the electronic theory of acids and bases.

A large number of different solvents are now used for all sorts of chemical reactions. It is possible to predict with some certainty what solvent is preferred for reactions of certain types. It is only recently that knowledge has been developed to the point where the distinctive character of non-aqueous solvents is being applied to certain definite phases of analytical chemistry. Although differences in solubility have long been employed to effect separations, it is only in the last few years that solvent character has been used to define acid-base behavior and that the very remarkable and useful differences of various solvents have been employed in routine analytical procedures.

WATER AS A SOLVENT

In order to characterize various non-aqueous solvents more precisely, it may be well to examine those particular properties of water which serve to distinguish it as a solvent from other materials. Nine characteristics are listed by Jander (3) as being responsible for the outstanding position which water occupies among solvents.

1. Water is available in greatest quantity.
2. Pure water is an excellent solvent for all kinds of substances, both electrolytes and non-electrolytes. Many other substances are better solvents for specific organic compounds, but none of them approaches water as a universal solvent for many different classes of substances.
3. Pure water is a poor conductor of electricity; it undergoes limited self-ionization into hydronium and hydroxyl ions.
4. Aqueous solutions of many substances, on the other hand, are excellent conductors of electricity.
5. Water takes part in hydration reactions involving coordination of water molecules with metallic ions and with various elemental and gaseous substances.

6. Neutralization reactions take place in the solvent water with facility. Neutralization reactions are closely related to the limited self-ionization of the solvent.

7. The phenomenon of hydrolysis is a characteristic reaction of water. Not only do dissolved salts undergo hydrolysis, but many substances, such as the acid chlorides, esters, and salts of extremely weak acids, react chemically with the solvent in such a way that the original solutes cannot be recovered directly therefrom.

8. The phenomenon of amphoterism is also listed as a specific characteristic of water. It is emphasized that a great many hydroxides and oxides are soluble in the presence of an excess of hydroxyl ion, and that the phenomenon of amphoterism is closely related to reactions of neutralization and of hydrolysis.

9. The solvent water appears to have the ability to convert potential electrolytes into true electrolytes. There are many substances such as sulfur trioxide, ammonia, tertiary amines, and hydrogen chloride which by themselves are non-electrolytes but react with the solvent water to give solutions which are excellent conductors.

Jander concludes this discussion in his monograph *Die Chemie in Wasserähnlichen Lösungsmitteln* with the statement that "the remarkable behavior of water is due largely to the structure of the water molecule, its dipole character, its small volume, and properties related thereto." The polar nature of water is responsible for its physical characteristics, "its exceptional solubilizing action, its ability to convert dissolved solutes into electrolytes and to effect their hydration." These remarkable properties of water, furthermore, are not shared by the other hydrides of the sixth periodic group. Only ammonia and hydrogen fluoride among the simple hydrides resemble water in these respects.

PHYSICAL PROPERTIES OF SOLVENTS

The superiority of water as a solvent is reflected more precisely through its exceptional and anomalous physical properties. The melting and boiling points of water are abnormally high; its heat of vaporization is also extraordinarily high, indicating extensive association in the liquid state. It possesses a high dielectric constant, which permits separation of ions and solution of ionic compounds. Water is a fluid medium of relatively low viscosity; ionic mobilities are correspondingly greater, and its usefulness as an electrolytic solvent is thereby enhanced. The physical properties cited for water serve to

distinguish good solvents from less desirable ones and also help to make possible the characterization of solvents with respect to their chemical and electrochemical behavior.

MELTING AND BOILING POINTS. These two physical properties define the limits of usefulness of a particular solvent under ordinary pressure conditions. Few substances whose boiling points lie below room temperature are usable as solvents, except where their availability and their distinctive character compensate for what might otherwise be considered a handicap. Such solvents as ammonia and sulfur dioxide are available in tremendous quantities, at a reasonable cost, and also have very unusual and desirable solvent characteristics. Both these substances are easily liquefied, with the result that they can be used in closed systems under pressure. Generally speaking, however, only those materials which can be handled without resort to unusual and difficult techniques are chosen as solvents for chemical reactions.

LATENT HEAT OF FUSION AND HEAT OF VAPORIZATION. Related to the melting and the boiling points are two further physical constants which in themselves define the energy necessary to bring about change in state from the solid to the liquid and from the liquid to the vapor. The heat of vaporization is specifically of interest with respect to another characteristic which is more difficult to evaluate, namely, the degree of association in the liquid state.

The ratio of heat of vaporization to the absolute boiling point, known as Trouton's constant, usually has a value of about 21.5 for normal liquids. Where the value is higher it is considered to be evidence that molecules of the liquid are associated into larger aggregates. Comparison of the physical properties of various non-aqueous solvents reveals that substances such as water, the alcohols, ammonia, and hydrogen fluoride possess abnormally high values for Trouton's constant. What is more significant, however, is that the compounds related to ammonia, water, and hydrogen fluoride, namely, phosphine, hydrogen sulfide, and hydrogen chloride, are apparently normal with respect to this particular relationship. Comparison of the boiling points and of the molecular heats of vaporization (4) of the hydrides of each of the groups beginning with nitrogen, oxygen, and fluorine reveals that the first members of each group possess unexpectedly high values (see Figures 1 and 2). These abnormalities disappear in the fourth group when a comparison is made between methane and the hydrides of silicon, germanium, and tin. Ammonia, water, and hydrogen fluoride are, therefore, substances which in the liquid state are not made up of simple molecules but of aggregates. Such aggre-

gates, in turn, must be dissociated through application of energy before the simple molecules can escape into the vapor state. High degree of association on the part of a solvent, as revealed from values for the heat of vaporization and for Trouton's constant, is further reflected

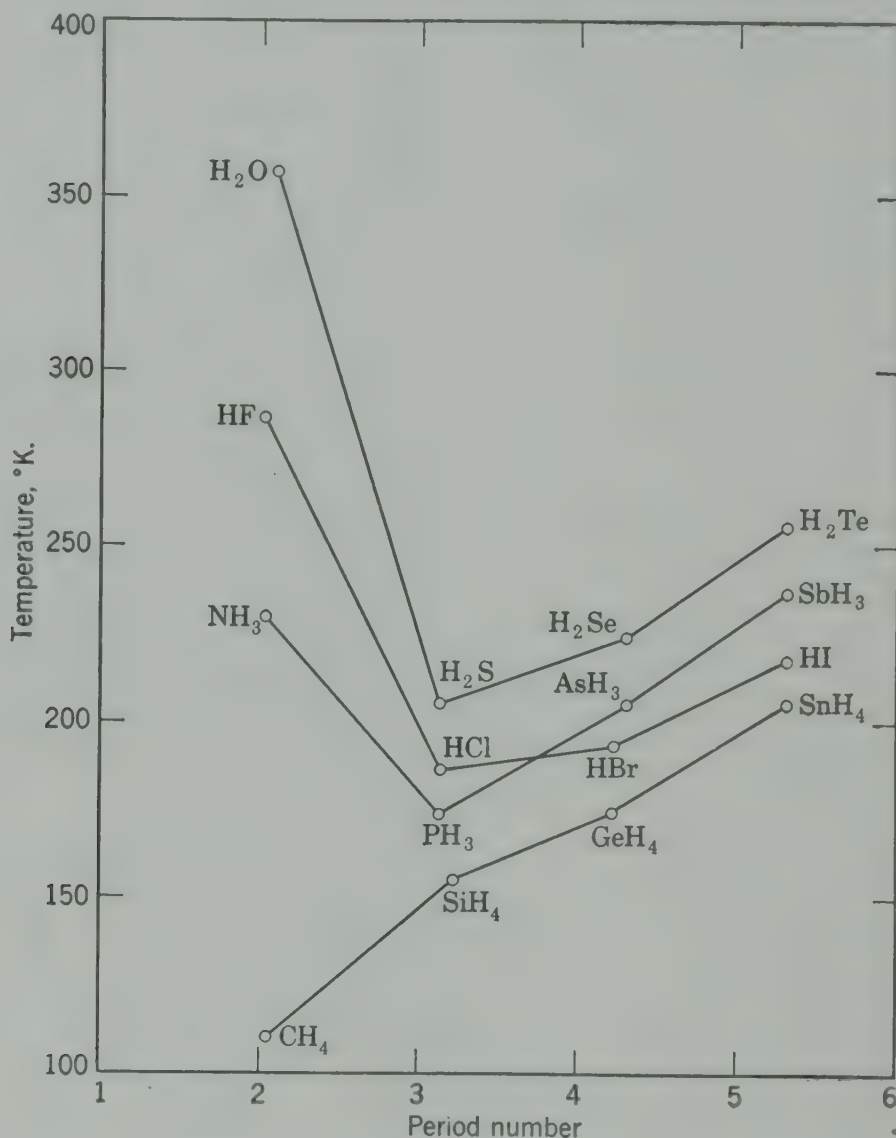


FIGURE 1. Boiling points of the volatile hydrides.

in a highly polar nature, high dielectric constant, and usually by outstanding ability to dissolve ionic compounds.

DIELECTRIC CONSTANT. Coulomb's law is given by the expression: $f = (1/\epsilon) \cdot (e_1 e_2 / r^2)$, where ϵ is the dielectric constant. The Nernst-Thomson rule is still applicable in a qualitative way, for it states that if the forces which hold a molecule together are electrical in origin, and we now recognize this to be the case, these forces are very much diminished when the molecule is surrounded by a substance of high inductive capacity. In order to separate charged particles, it is

necessary to interpose between them, or to surround one or both of them by a solvent layer, which reduces their attraction for each other. The lower the dielectric constant of the medium, the greater is the associating power of the ions for each other and, consequently, the greater is the tendency for such ions to aggregate into inactive ion pairs or even larger complexes. A medium of high dielectric constant, such as water, will generally serve as a good solvent for ionic compounds. Even liquid ammonia is a fairly good solvent for ionic com-

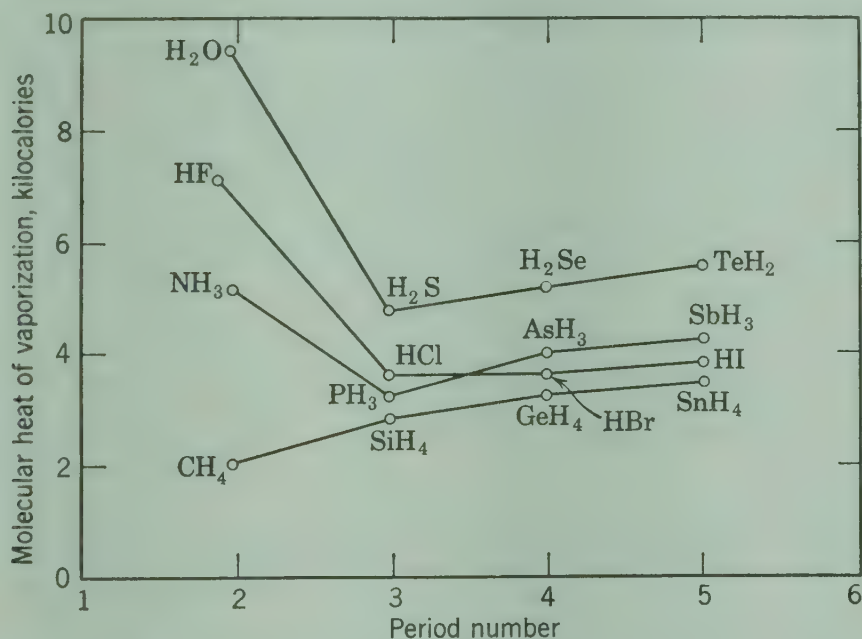


FIGURE 2. Molecular heats of vaporization of the volatile hydrides.

pounds, in spite of the fact that its dielectric constant is very much smaller than that of water.

It should be pointed out in this connection that solvents of high dielectric constant are invariably highly polar. This characteristic leads, in turn, to association in the liquid state, together with attendant anomalous and abnormal physical properties.

VISCOSITY. Mention is made of this particular physical property, since it does influence the usefulness of a solvent. Viscosity very profoundly affects the mobility of ionic species and the conductance of electrolytes in a particular solvent (5). Quite apart from this physico-chemical characteristic, however, is the fact that solvents of low viscosity are easier to handle and to process. Both liquid ammonia and water possess high fluidity. Anhydrous sulfuric acid, on the other hand, is an extremely viscous medium; precipitation and crystallization are more difficult to carry out in it and filtration operations are not as readily effected.

CLASSIFICATION OF SOLVENTS (6)

Possible solvents can be classified and, in turn, can be differentiated on the basis of a number of rather obvious properties. Each method of classification has its usefulness. *Chemical character* is probably the most obvious criterion for distinguishing between solvent types although it is of less importance than a related classification based on the concept of *parent solvents*. The behavior of certain acids and bases is determined largely by the protophylic nature of the solvent, that is, by the tendency on the part of the solvent to coordinate the hydrogen ion to react with a potential proton donor to form the solvated hydrogen ion. A classification which depends on the manner in which electrolyte strength is affected places all solvents in one of two categories: *differentiating* and *leveling solvents*. A *utilitarian* classification takes into account economic factors as well as solvent properties.

CHEMICAL CHARACTER. It is quite desirable to classify solvents on the basis of distinctive groups which may be present in a molecule. By far the most useful solvents are the hydrides. They are very often called protonic solvents, although it should be pointed out that not all hydrogen-containing solvents dissociate the proton as is implied by this particular designation. Next in order of importance are the hydroxylic solvents which resemble water, but in which hydrogen is replaced by some organic radical. They include the alcohols and the polyhydroxy compounds and other oxygen-containing solvents such as the ethers, esters, aldehydes, and ketones. The nitrogen-containing solvents constitute a large and important group. Of these, only ammonia has been investigated thoroughly. Substituted amines and polyamines, which resemble ammonia in much the same way that alcohols resemble water, are poorer solvents than ammonia for ionic compounds, but better solvents for organic materials. Reference should also be made to such interesting solvents as pyridine, which from the Franklin point of view may be looked upon as a cyclic ammono ether, and hydrazine, a solvent of theoretical interest and potentially of considerable importance from the practical point of view.

Solvents which are acids include such compounds as sulfuric acid, acetic acid, formic acid, and hydrogen fluoride. Related to them are the acid chlorides such as carbonyl chloride, phosphorus(V) oxychloride, selenium(IV) oxychloride, thionyl chloride, and sulfuryl chloride, all of which have been evaluated to some extent for their solvent characteristics. Sulfur dioxide and sulfur trioxide may also be included in

this category. Although sulfur dioxide has received considerable attention, practically nothing has been done with sulfur trioxide as a solvent. It is now available as a stabilized liquid.

The very large group of inert solvents which are employed in synthetic organic chemistry include the hydrocarbons and their halogenated derivatives. They are non-polar, or only slightly polar. They are generally very poor solvents for ionic compounds, but excellent solvents for covalent and non-polar compounds. Ionic reactions cannot be carried out readily in solvents of this type.

It is possible to predict solubility trends in solvents of the same chemical type, a fact which has been recognized from a comparison of solubility relationships in water and related hydroxylic solvents. Replacement of hydrogen in water by organic radicals reduces solvent ability for inorganic compounds, but increases the tendency of the resulting substances to become better solvents for organic compounds. Nitrogen compounds are generally more soluble in ammonia and nitrogen-containing solvents; oxygen compounds, in turn, are more soluble in water and the alcohols. It is also to be expected that completely non-polar substances are more soluble in organic solvents which are non-polar and inert.

PARENT SOLVENTS. Many of the compounds which are to be discussed as solvents may be regarded as parent substances of systems of acids, bases, and salts. This concept is taken up in more detail in Chapter 2. Suffice it to point out here that this particular concept is of importance in predicting the probable behavior of solutes in various solvents. The solvent system concept was first promulgated by Franklin, who recognized that a large number of nitrogen compounds may be related to ammonia as the parent substance in the same way that the corresponding oxygen compounds are related to water. Compounds containing the amide, the imide, and nitride groupings were considered to be similar to substances containing hydroxyl and oxo groups or ions. Experimental verification of this point of view by a study of reactions in liquid ammonia led eventually to its extension to other protonic systems. In some instances, the parent substances are themselves very poor solvents, but use of the concept makes possible classification of compounds which are related generically to such a parent solvent.

The aquo and the ammonio systems, in which water and ammonia represent the parent solvents, have been studied thoroughly. The parent solvent concept has been shown to be useful in each of these instances not only for purposes of classification, but also for the

prediction of the nature of reactions which take place in each. Sulfur compounds have in like manner been related to hydrogen sulfide as a parent substance, but hydrogen sulfide is such an extremely poor solvent that the extension of this concept is practical only as a means of classification. Other solvents which have been evaluated experimentally from this point of view are liquid hydrogen cyanide, hydrazine, formamide, and anhydrous nitric and acetic acids. All these are protonic solvents and will dissociate the proton to undergo self-ionization in accordance with the following type equation:



However, consideration of non-aqueous solvents as parent substances of systems of compounds has not been limited to protonic solvents. Systems of acids, bases, and salts have been derived from sulfur dioxide, carbonyl chloride, selenium(IV) oxychloride, and even liquid iodine. Each of these substances is assumed to undergo self-ionization to give characteristic "acid-analogous" and "base-analogous" type ions. Solutes which contain such "analogous" groups may, therefore, be expected to exhibit their true behavior in the parent solvent to which they are related.

PROTOPHYLIC NATURE. One of the most important characteristics of any solvent has to do with its ability to form the onium ion, either by self-ionization or by reaction with some potential proton donor. Solvents fall into four classes when differentiated on the basis of their ability to coordinate the hydrogen ion:

1. Basic solvents are those which form the onium ion readily. Basic solvents include ammonia and the amines, hydrazine and hydrazine derivatives, cyclic nitrogen compounds such as pyridine, and even the low-molecular-weight ethers.

2. Acidic solvents include such materials as sulfuric acid, acetic acid, and hydrogen fluoride. None of these substances is capable of forming a very stable combination with the hydrogen ion. Acidic solvents tend to dissociate the hydrogen ion readily, whereas basic solvents tend to coordinate with the hydrogen ion and metallic ions to form the solvated cations. Proton-containing acidic solvents may be presumed to solvate the anion through hydrogen bonding. Hydrogen fluoride attaches itself quite strongly to the fluoride ion, with the formation of a very strong FHF bond. Although it has not yet been proved to be the case, it is entirely possible that acetic acid and sulfuric acid form solvates through hydrogen bonding with the anion.

3. Amphiprotic solvents are capable of acting as electron pair donors, but will under proper circumstances also dissociate the proton to a dissolved solute. Water and the hydroxylic solvents are the outstanding examples of such classes of materials. Ammonia is also amphiprotic. Water is a highly polar compound. The point of attachment (or orientation) of a water molecule to a cation is through the electron pair (the negative end) on the oxygen atom. Water, therefore, coordinates with the proton quite effectively and readily. It also forms stable aquated cationic complexes with many metallic ions. In competition with poorer proton donors than itself, water will also release the proton to such basic materials. Molecules such as ammonia and anions such as the cyanide and carbonate ions are typical proton acceptors in aqueous solution.

4. Aprotic solvents include the inert materials which have no affinity for the proton and/or which are incapable of dissociating the proton. It is perhaps incorrect to assume that there is any such thing as an inert solvent. On the other hand, in relation to those other materials which have been designated above as basic, acidic, or amphiprotic solvents, it must be recognized that hydrocarbons and the halogenated hydrocarbons are aprotic in nature and will not affect strongly the properties of either a base or an acid which may be dissolved in them.

Classification of solvents on the basis of their protophylic nature is especially useful in connection with the Brönsted-Lowry concept which defines the behavior of hydrogen-containing compounds as acids. Whether or not a substance will behave as an acid or as a base depends upon the character of the solvent. Urea is very weakly basic in aqueous solution, but behaves as a weak acid in liquid ammonia. Many substances which are weak bases in aqueous solution exhibit enhanced basic character when dissolved in an acidic solvent. From a practical point of view this is quite important since salts of weak acids can be prepared most readily in basic solvents, whereas salts of weak bases can be synthesized most readily in acidic solvents.

DIFFERENTIATING AND LEVELING SOLVENTS. Electrolyte strength is often specified merely in terms of behavior of a particular substance in aqueous solution. There are many factors which influence the strength of an electrolyte, yet these same factors do not necessarily play comparable roles when the same solute is placed in a non-aqueous medium. Solvents are, therefore, frequently classified on the basis of the behavior exhibited by typical electrolytes in them. Those in which such reference electrolytes are equally strong are known as leveling

solvents. Those in which differentiation in strength of electrolyte occurs are known as the differentiating solvents.

Walden (7) was one of the first to point out the very unusual effects which various solvents have upon certain substances designated as strong electrolytes on the basis of their behavior in water. Table 1

TABLE 1
DIFFERENTIATING AND LEVELING SOLVENTS

(α -values for reference electrolytes in various solvents at a dilution of 2000 liters)

<i>Solvent</i>	<i>Electrolytes</i>		
	<i>Tetraethylammonium</i>	<i>Diethylammonium</i>	
	<i>Picrate</i>	<i>Picrate</i>	<i>Chloride</i>
H ₂ O	0.99 = 100 *	98	98
CH ₃ OH	0.95 = 100	..	97
C ₂ H ₅ OH	0.89 = 100	..	99
CH ₃ CN	0.95 = 100	95	33
(CH ₃) ₂ CO	0.88 = 100	86	11
CH ₃ COC ₂ H ₅	0.85 = 100	61	6
C ₅ H ₅ N	0.74 = 100	72	5
C ₂ H ₄ Cl ₂	0.47 = 100	1	0

* α -values have been set as equal to 100 for tetraethylammonium picrate to permit more direct comparison.

gives the α -values at a dilution of 2000 liters for tetraethylammonium picrate, diethylammonium picrate, and diethylammonium chloride in a series of different solvents. The α -values represent the classical degree of dissociation calculated from conductance data at the indicated dilution, compared with the extrapolated values at infinite dilution. Inspection of the data given in this table reveals that water, methanol, and ethanol are leveling solvents, whereas acetonitrile, acetone, methylethyl ketone, pyridine, and ethylene dichloride may be regarded as differentiating solvents. In the first three of these solvents, the three reference electrolytes are of approximately equal strength, as determined from their conductance values, but a profound differentiation occurs when these same substances are dissolved in the other solvents.

Most striking is the fact that differentiation in the electrolyte strength of acids occurs in glacial acetic acid as solvent. Hydrogen acids dissociate the proton in acidic solvents only to the extent that they themselves are intrinsically capable of doing so; acidic solvents are poor proton acceptors. Perchloric acid, for instance, is a relatively

strong electrolyte in 100% acetic acid. Sulfuric acid and hydrogen chloride are much weaker electrolytes, yet all three of these substances are apparently of equal strength in aqueous solution. The whole subject of differentiation in electrolyte strength, especially as it refers to acids, and possibly bases, as a function of the solvent, is one which demands considerably more study and investigation than it has received thus far.

UTILITY. There are a number of factors which, in addition to those discussed above, determine the usefulness of a solvent. Physical properties of an objectionable nature would naturally militate against use of a particular solvent. Availability would create more incentive towards investigation and use of a particular solvent medium. Economic factors would also tend to influence more intensive investigation of a material, especially if its practical uses were envisaged.

Chemical stability towards oxygen, water vapor, and carbon dioxide of the atmosphere is a factor of some importance. Basic solvents must obviously be protected from the atmosphere so that carbon dioxide absorption will not bring about their deterioration. The same is true of such solvents as sulfuric acid, acetic acid, and anhydrous hydrogen fluoride, all of which absorb moisture from the atmosphere quite readily. It is surprising what a tremendous influence a trace of moisture will occasionally have on solvent ability and solubility relationships.

Perhaps of even more importance than some of these properties is the hazard or toxicity associated with the use of a particular solvent. Ammonia is a rather toxic material, and care must therefore be taken in working with it. Anhydrous hydrogen fluoride is also a solvent which must be handled with considerable care. The same is true of liquid sulfur dioxide; but the scientist in quest of fundamental, theoretical knowledge has not permitted inherent danger to block his path. Even solvents such as anhydrous hydrogen cyanide and liquid hydrogen sulfide have been subjected to careful study.

When all these various factors are taken into consideration, it becomes quite apparent that solvents which are useful as media for chemical reactions are relatively few in number. They include: (a) *water-like solvents*, such as the alcohols, ethers, polyethers, ketones, and esters; (b) *nitrogen-containing solvents*, such as amines, diamines, polyamines, ethanolamines, pyridine, hydrazine, nitriles, and the lower acid amides such as formamide and acetamide; (c) solvents which are *acids*, for example, acetic acid, formic acid, hydrogen fluoride, and sulfuric acid; (d) *miscellaneous solvents*, such as sulfur dioxide, inorganic acid chlorides, hydrocarbons, and their derivatives.

TYPE REACTIONS IN NON-AQUEOUS SOLVENTS (6)

There are certain characteristic reactions whose course is determined largely by the nature of the solvent. This particular qualification is necessary since oxidation-reduction reactions are in a large measure reactions which depend upon the solute; the solvent plays only a secondary role. Reactions which are, however, markedly influenced by the solvent include (a) metathetical and neutralization reactions; (b) reactions of solvolysis; (c) reactions of solvation.

METATHETICAL AND NEUTRALIZATION REACTIONS. It may be asked why metathetical reactions are included among those for which the solvent is largely responsible. In general, only those metathetical reactions are considered which involve precipitation. Reactions which result in the formation of insoluble precipitates are the basis for many qualitative and quantitative separations in water. Since solubility relationships differ in various solvents, it is not at all surprising to find that metathetical reactions may take an altogether different course in certain non-aqueous solvents than they do in water. The interaction of solutions of silver chloride and barium nitrate in liquid ammonia results in precipitation of barium chloride. The addition of sulfuric acid to a solution of copper nitrate in acetic acid results in the precipitation of anhydrous copper sulfate. Both ammonium sulfate and ammonium nitrate are soluble in water. In liquid ammonia, on the other hand, ammonium sulfate is insoluble, whereas ammonium nitrate is extremely soluble. Separations can, therefore, be effected by employing appropriate metathetical reactions.

Reactions involving salt formation by the interaction of an acid and a base also vary from solvent to solvent, for the simple reason that the solvent may change the acidic or basic character of a solute. Sodium acetate is a base in glacial acetic acid; ammonia is likewise a strong base in glacial acetic acid. Substances which behave as acids in aqueous solution may have altogether different character in some other solvent. Potassium acid phthalate is a useful acidimetric standard in aqueous solutions, but can be used as a base standard in acetic acid. A solution of potassium acid phthalate in glacial acetic acid is the equivalent of a solution of potassium acetate in this particular solvent. The material which serves as a primary acidimetric standard in aqueous solution becomes a primary base standard by reaction with the solvent glacial acetic acid.

Frequent references will be made to the unusual properties of certain basic solvents, particularly liquid ammonia, which permit forma-

tion of salts whose existence in contact with water is impossible. The nitrogen derivatives of the organic and inorganic acids exhibit varied character in aqueous solution. Urea, guanidine, cyanamide, cyanic acid, and melamine are all nitrogen derivatives of carbonic acid. Their behaviors in aqueous solution differ markedly. In liquid ammonia, however, each of these substances is capable of reacting as an acid with metallic amides and, in some cases, with metallic ions, to form salts. Guanidine, for instance, is a strong base in aqueous solution. This is equivalent to saying that guanidine competes with the solvent water for the proton which the solvent is capable of dissociating. In liquid ammonia, however, ammonia competes with the solute guanidine for the proton which guanidine itself is capable of releasing. Metallic salts of guanidine and related compounds can, therefore, be prepared in the solvent ammonia. As might be anticipated, such products undergo immediate decomposition and solvolysis when brought into contact with water and more acidic solvents.

SOLVOLYTIC REACTIONS. When the dissolved solute reacts with the solvent in such a way that the normal anion and cation concentrations of the solvent are changed, the solute is said to have undergone solvolysis. Although it is not necessary for such reactions to be carried out in the solvent itself, it is only under such circumstances that the true nature of the solvolytic products becomes apparent. Reactions of solvolysis can be carried out in the vapor state, in inert solvents, and in the solvent itself.

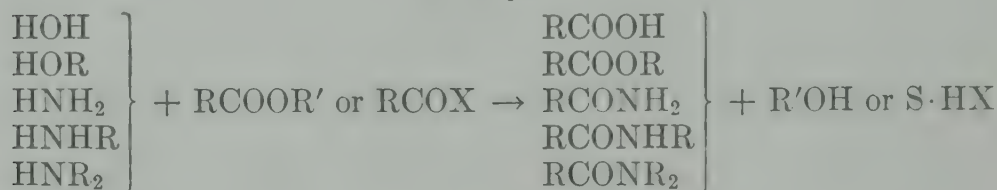
Solvolytic reactions constitute the most important type reactions which can occur in solvent systems. It makes little difference whether water, ammonia, an alcohol, a primary or a secondary amine undergo reaction with an organic or an inorganic compound containing a reactive grouping. Compounds are obtained in all instances which are formally related in the same manner to each of the solvolytic agents as parent substances. Examination of some typical reactions given in Table 2 shows that solvolytic replacement of the active chlorine atoms in phosphorus(V) oxychloride results in the formation of two groups of compounds, each member of which is formally related to each of the others. The reaction of an organic ester or an acid chloride with these same parent solvents likewise leads to similar solvolytic products. This point of view can be extended to cover reactions involving hydrazine, hydroxylamine, and their N-substituted derivatives, all of which can also serve as solvolytic agents. It is important to recognize that the essential nature of the reaction is the same in each case. When, therefore, reference is made to solvolytic reactions involving the use of

TABLE 2
SOLVOLYTIC REACTIONS

A. Inorganic



B. Organic



ammonia to effect the preparation of nitrogen (ammono) compounds of some of the common inorganic acids, it may be well to remember that the corresponding N-substituted derivatives may also be prepared by using a primary or secondary amine as solvolytic agent. In like fashion, if a reaction of hydrolysis is known to occur, it may be anticipated that the corresponding reactions of alcoholysis, that is, the reaction of alcohol upon the same material, may lead to analogous compounds.

It is preferable to speak of solvolytic reactions in all these instances rather than to use the special terminology which has been developed by proponents of various solvent systems of compounds. Reactions of ammonolysis, hydrazinolysis, aminolysis, and alcoholysis are solvolytic reactions in which ammonia, hydrazine, an amine, and an alcohol have been employed as reagents, respectively.

It should be emphasized again that all these solvolytic reactions, when carried out in the parent solvent, do, in effect, bring about the development of either an acidic or a basic solution. Thus, for instance, a reaction of hydrolysis involving phosphorus(V) oxychloride leads to the formation of phosphoric and hydrochloric acids. The pH of the solution is thereby decreased, indicating that the equilibrium concentrations of hydrogen and hydroxyl ions formed by auto-ionization of the solvent have been disturbed. Corresponding reactions of ammonolysis result in the formation of a hypothetical phosphoryl triamide and of ammonium chloride. Ammonium chloride is an acidic substance in liquid ammonia, and for that reason its presence in solution, regardless of the behavior of the phosphoric acid analog, imparts acid character to the solution. In other words, the solute has re-

acted with ammonia as the solvent to increase the ammonium ion concentration above that which characterizes the solvent itself.

SOLVATION REACTIONS. The process of solvation results in the attachment of the solvent molecule to the cation, the anion, or a molecule of a solute, either by coordination or by hydrogen bonding. Products of varying stability are formed. The process of solvation is closely related to the process of solvolysis, as interaction of solvent with solute to form a solvate is often accompanied by a change in the concentration of either the acid or the base analog ion.

The process of solvation is closely related to the process of solution. In order to bring about the solution of an ionic crystalline compound it is necessary to interpose solvent layers around each of the ions so that their attraction for each other is reduced. There thus appears to be a close relationship between the physical properties of the solvent molecule such as the dielectric constant, the degree of association and the polarity, and its ability to solvate an electrolyte and to yield a conducting solution. The process of solution of an ionic compound is one in which the shielding of the charged particles by the dipoles of the solvent can take place. Solvation of cations presumably occurs through a process of coordination, in which the solvent molecule represents the electron pair donor and so orients itself as to effect a shielding of the positively charged ion. The higher the charge on a cation, the more readily solvated is such a cation and the more stable is the resulting cationic solvate.

Solvation of anions is generally neglected in a consideration of the process of solution; however, the anion is always an electron pair donor and could, therefore, solvate non-hydrogen-containing solvents whose molecules can be represented by electron-deficient structures. In hydrogen-containing solvents, however, the process is believed to be one in which hydrogen bonds are formed. These bonds are much weaker than the coordinate bonds by which solvent molecules are attached to the cation. The process of solvation of an anion by water may, therefore, be considered to involve orientation of the water molecules towards the anion through the positively charged hydrogen end of the water dipole. The over-all effect is that both cations and anions are solvated in any system of this sort.

Although less can be said concerning solvation by non-hydrogen-containing substances, it is the considered opinion of the authors that anion solvation most certainly occurs in liquid sulfur dioxide as a solvent. It also seems highly probable that solvation in acidic solvents, such as sulfuric acid, acetic acid, and hydrogen fluoride, takes place through a process of anionic hydrogen bonding.

The process of solvation is definitely connected with the existence of stable solvates, that is, compounds containing solvent of crystallization. Where water is the solvent, hydrates are formed. If ammonia is the solvent, ammoniates are obtained; where these are very stable, such as the cobalt(III) compounds, they are usually designated as ammines. Hydrazinates, hydroxylamates, alcoholates, etherates, and a great many other compounds of this type are known. Rather than develop a special terminology for each it is preferable to speak of them as solvates.

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ACIDS AND BASES

No classes of substances vary more profoundly in behavior with respect to the solvent than do those compounds which are designated as acids and bases. Terminology and definitions were relatively simple so long as water was considered to be the only "ionizing" solvent. According to Arrhenius, acids are substances which yield the hydrogen ion in solution, whereas bases produce the hydroxyl ion. Water is merely the solvent medium and serves to bring about the dissociation of acid and base (or salt) molecules into ions. Although this older generalization can still be regarded as of greatest practical interest, it is limited specifically to water and cannot be applied to the multitude of other solvents which have been subjected to study since the beginning of the twentieth century.

At least three other concepts have been advanced with respect to acid-base relationships to include the work which is being done in non-aqueous solvent chemistry. The *solvent system concept*, first suggested by Franklin, was originally limited to water and ammonia but has since been extended to other protonic solvents and also to non-protonic media. The *protonic concept* advanced by Brönsted and by Lowry represents a refinement of the Davy-Liebig hydrogen theory of acids. Acids are proton donors whereas bases are proton acceptors. The *electronic theory*, promulgated by Lewis, represents the most recent approach to the subject. Attempts have, of course, been made to limit or extend each of these general definitions. Essentially, however, there are four fundamental concepts, of which only three apply to solvents in general, since the Arrhenius definition holds strictly only for aqueous solutions.

It may be appropriate in this connection to call attention to a related field of effort which has only recently been subjected to study. Acid-base definitions which hold for systems at ordinary temperatures have been shown by Audrieth and co-workers to be applicable to many non-aqueous, non-solvent reactions in the fused state and at higher temperatures. European investigators, notably Lux and Flood, have

made a special study of oxide systems at higher temperatures and have come to the conclusion that acid-base relationships in such media involve the transfer of oxygen from one state of polarization to another. Since such high-temperature non-aqueous media are of great practical value, acid-base relationships in such systems are taken up in detail in Chapter 14.

HISTORICAL DEVELOPMENT OF ACID-BASE CONCEPTS (1, 2, 3)

The historical development of concepts defining acid-base relationships represents "an interesting chapter in our intellectual history for it concerns a complex problem whose chronological development we may follow without a gap for several hundred years." It was not until early in the seventeenth century that the first definitions for these classes of substances appear in chemical writings. It was Glauber (1604–1668) who promulgated what is now known as the *dualistic concept* for salts and who first made use of synthetic methods to demonstrate that such substances can be obtained by the combination of acids and bases. He came to the conclusion that "every volatile base such as ammonia may be contrasted chemically with every volatile acid." He demonstrated that "the volatile base [ammonia] possesses the same chemical properties in solution as alkaline potash solutions [potassium carbonate], since both precipitate dissolved metallic salts in the same way." Experimental proof for the dual nature of potassium nitrate was presented by Glauber in the following words: "The liquor fixus [KOH , K_2CO_3] and the spiritus acidus nitri [HNO_3] are in their nature totally unlike, foes and adversaries of each other . . . and when the two are brought together again . . . and the one kind has overcome and destroyed the other, neither a fiery liquor nor a spiritus acidus is to be found in their dead bodies, but the same has again been made as both were before and from which they were derived, namely, ordinary saltpeter."

Boyle in England and Lémery in France were contemporaries of Glauber, and, like him, also made a special study of acids and bases. Each one had available the same background and information, and each one employed experimental criteria for the characterization of acids, bases, and salts. Boyle (1627–1691) describes acids as substances which (a) dissolve many other substances, (b) precipitate sulfur from its solution in alkalies, and (c) turn blue plant dyes red. It is evident that Boyle recognized the dualistic nature of salts since he makes reference to the fact that the properties of acids are lost on

contact with alkalies. L  mery (1645–1715) was even more ingenious than his contemporaries in characterizing acids and bases. Since acids possess a biting taste and alkalies impart a smooth feeling to the skin, he came to the conclusion that an acid is composed of pointed particles which are in rapid agitation, whereas an alkali is composed of rounded particles. He recognized that the distinctive properties of these two classes of substances disappear when brought into contact with each other. He, therefore, elaborated his definition by postulating that the rounded particles of alkali contain pores into which the pointed particles of the acid might fit so that their further movement is prevented.

The history of philosophy reveals that practitioners of science have always attempted to explain detailed phenomena in terms of a more inclusive, over-all concept, which in their times represented the ultimate in theory. When Stahl promulgated the *phlogiston theory* to explain the process of combustion, it was only logical that an effort should have been made to use this new universal concept as a basis for a more general definition of acids and bases. These classes of substances were believed to form from the elements by loss of the combustible principle. Experimental characteristics of acids and bases and the dualistic nature of salts were recognized, however, even though the phlogiston theory was accepted generally. Acids were defined by Lewis (1856) as “all those things which taste sour upon being reduced to a proper degree of strength” and “which effervesce with chalk and with salts of vegetables prepared by incineration; and with such like substances form a neutral salt. They are likewise distinguished from alkalis by turning syrup of violets red.” This same English chemist states that “an alkali is any substances which being mixed with an acid, ebullition and effervescence ensue thereon and which afterwards forms a neutral salt. They are likewise distinguished from acids by turning syrup of violets green.”

With the discovery of oxygen by Priestley and Scheele and the recognition by Lavoisier of the true nature of combustion the science of chemistry entered a new era. Emphasis was placed upon the composition of matter rather than upon phenomenological properties. Mechanisms and patterns of behavior were now interpreted on the basis of whether or not a substance contained oxygen. Oxygen had been found to combine with many non-metallic substances (or radicals) to give acids. This led Lavoisier to advance the *oxygen theory* based on the assumption that all acids consist of two parts, one of which is oxygen and the other a so-called acidifiable radical.

However, the oxygen theory which seemed so perfectly logical to Lavoisier and his contemporaries was found to be wanting as new facts were uncovered. After a considerable amount of work with "oxymuriatic acid," Davy came to the conclusion that "we have no more right to say that oxymuriatic acid contains oxygen than to say that tin contains hydrogen. The name should express things and not opinions. Until a body is decomposed, it should be considered as simple." Davy subsequently demonstrated that it is chlorine which is combined with hydrogen in hydrochloric acid and that oxygen cannot be responsible for the acidic nature of this compound. Thus was born Davy's *hydrogen theory*.

There were those, however, who even then felt that an acid could not be properly defined in terms of its composition and that it was useless to characterize such substances by designating some element as the acidifying principle. One of these dissenters was Gay-Lussac, who in 1814 came to the remarkable conclusion that "one is forced to explain acidity by the fact that it satisfies alkalinity, because alkalinity and acidity are two correlated and inseparable properties." Nevertheless, the hydrogen theory finally came to be accepted as additional hydrogen acids, such as prussic acid, thiocyanic acid, the remaining hydrogen halides, and the acidic hydrides of selenium, sulfur, and tellurium were discovered. It is interesting to point out, however, that a compromise was necessary for these non-oxygen-containing acids were specifically designated *hydracids*.

It remained for Liebig (1803–1873) to reconcile existing theories by calling attention to the fact that all acids possess similar properties whether they are hydracids, oxygen acids, or organic acids. Liebig proposed the idea of a replaceable hydrogen atom as the definitive characteristic of acids. He also introduced the term *acid radical* as it is used today, and he distinguished between *monobasic*, *dibasic*, and *tribasic* acids, depending upon whether one, two, or three hydrogen atoms may be replaced by metals.

A new experimental approach was brought to bear upon this problem by Faraday. To him, all acids, bases, and salts were electrolytes because aqueous solutions of these classes of substances were found to conduct the electric current.

Most of the classical electrochemists of the middle nineteenth century continued to study the behavior of electrolytes in water solutions. A few, however, undertook to investigate the electrochemical behavior of so-called electrolytes *per se*, such as liquid hydrogen chloride and liquid ammonia. When these were found to be non-conductors, the assumption was promptly made that only in water do these substances

possess characteristic chemical and electrochemical properties, and that only in water is it possible to effect ionic reactions.

The stage was, therefore, logically set for Arrhenius (1884) in presenting his theory of electrolytic dissociation to place specific emphasis on the role of water as an ionizing solvent. According to Arrhenius, no compound can function as an acid *per se*. Only when dissolved in water does it become a conductor, and only in water is it dissociated to give the positively charged hydrogen ion which now came to be regarded as the distinguishing characteristic of acids. Potassium hydroxide and ammonia are bases only because water brings about either dissociation, or reaction followed by dissociation, to give hydroxyl ion in solution.

The limitations of the Arrhenius theory with respect to its emphasis on water as an ionizing medium were soon recognized by two groups of chemists, who, at the turn of the century, began work on the chemistry and electrochemistry of non-aqueous solutions. The European school under the leadership of Paul Walden had initiated such activities by an investigation of the conductance of electrolytes in sulfur dioxide. Contemporary activity was initiated in this country by Cady, Franklin, and Kraus in their study of liquid ammonia as a solvent and reaction medium. Results of this early work in non-aqueous solvents were destined to affect profoundly not only future developments in synthetic inorganic and organic chemistry but also modern theory as well. A new period in the development of the acid-base concept was ushered in with the more active interest in the behavior of solvents other than water, and older ideas about acids and bases most certainly had to be revised. As more and more data were accumulated, an effort was made to explain phenomena in terms of the parent solvent, with the result that the solvent theory of acids, bases, and salts was set up. Subsequently, both Brönsted and Lowry attempted to explain phenomena in a wide variety of hydrogen-containing solvents by proposing the so-called protonic theory. Each of these concepts was in itself found to be too specific, with the result that the electronic theory of structure of matter was applied by G. N. Lewis (4) to account for the behavior of acids and bases.

Before discussing in some detail each of the various concepts which have been proposed to account for acid-base relationships, it might be well to refer to the fact that the terms *acid* and *base strengths* as applied to protonic substances have been used very loosely by various authors. In view of the many different shades of meaning attached to these terms by different authors and the emotional intensity with which each adheres to his own interpretation, we have made an effort

in our presentation to dispense very largely with these terms and to limit ourselves to more specific concepts which are defined herewith: (a) *Intrinsic acidity* (or *basicity*) of a substance represents its inherent tendency to lose (or gain) a proton. This is independent of the solvent and depends only on the acid or base. (b) *Acidic* (or *basic*) *character* of a solute in a given solvent is defined as the tendency to lose a proton to (or gain a proton from) the particular solvent in question. This depends upon the relative affinity of solute and solvent for protons. It is particularly important in the solvent system concept. (c) *Strength* as an *electrolyte* is characterized by the degree of dissociation and depends upon both solute and solvent and especially upon the dielectric constant of the solvent.

SOLVENT SYSTEM CONCEPT (5, 6)

Miscellaneous observations on the behavior of substances in liquid ammonia had been made late in the nineteenth century by several early workers, but the specific relationship of nitrogen compounds to liquid ammonia as a parent solvent had not been recognized. Franklin and Kraus began their first studies by testing qualitatively the solubilities of a large number of inorganic and organic compounds in liquid ammonia. They then found that distinctive metathetical reactions could also be carried out in liquid ammonia. As more and more experimental material was brought to light, it became apparent that many nitrogen compounds are related to ammonia as the parent substance in the same manner as analogous oxygen compounds are to water. It was furthermore suggested that ammonia could undergo limited self-ionization into hydrogen and amide ions:



It, therefore, became obvious that the amide and hydroxyl ions might be considered analogous groups with respect to the corresponding parent substances. The extension of these formal analogies resulted in the development of the nitrogen system of compounds (7). To differentiate between oxygen and nitrogen compounds while emphasizing the analogy between them, derivatives of water were designated as *aquo compounds* whereas those of ammonia were labeled *ammono compounds*. These relationships are illustrated in Table 3, in which corresponding aquo and ammono compounds are listed side by side.

TABLE 3
AQUO AND AMMONO COMPOUNDS

<i>Ammono Compounds</i>	<i>Corresponding Aquo Compounds</i>
KNH_2 , potassium amide	KOH
PbNH , lead imide	PbO
Hg_3N_2 , mercuric nitride	HgO
$\text{K}_2\text{Zn}(\text{NH})_2 \cdot 2\text{NH}_3$, potassium ammono zincate	$\text{K}_2\text{Zn}(\text{OH})_4$
HgNH_2Cl , ammonobasic mercuric chloride	$\text{HgO} \cdot \text{HgCl}_2$
$\text{C}(\text{NH})(\text{NH}_2)_2$, guanidine	CO(OH) ₂
H_2NCN , cyanamide	
$\text{CO}(\text{NH}_2)_2$, urea	
$\text{HN} \cdot \text{N}_2$, hydrazoic acid	HONO ₂
$\text{NH}_2\text{SO}_3\text{H}$, sulfamic acid	SO ₂ (OH) ₂
$\text{SO}_2(\text{NH}_2)_2$, sulfamide	
CH_3CONH_2 , acetamide	CH ₃ COOH
$\text{CH}_3\text{C}(\text{NH})(\text{NH}_2)$, acetamidine	
CH_3NH_2 , methylamine	CH ₃ OH
$(\text{C}_2\text{H}_5)_3\text{N}$, triethylamine	$(\text{C}_2\text{H}_5)_2\text{O}$

It is obvious that such formal systems of compounds can be set up for many other parent substances. For ammonia, however, it is significant that the indicated analogies have been verified experimentally. Nitrogen compounds such as those listed in Table 3 exhibit, in liquid ammonia, the characteristic properties suggested by the behavior of the corresponding oxygen compounds in aqueous solution. Ammonium salts were found to behave as acids in liquid ammonia, just as hydronium salts act as acids in aqueous solution. Metallic amides such as potassium amide were actually found to behave as bases in liquid ammonia.

Perhaps even more striking was the extension of these formal analogies to the nitrogen derivatives of the non-metallic elements. Thus, for instance, urea, cyanamide, and guanidine may be considered formally to be ammono carbonic acids, that is, nitrogen analogs of carbonic acid. The behavior of each of these substances in aqueous solutions is distinctly different. Urea is a weak base; guanidine is a rather strong base; cyanamide is a relatively weak acid. In liquid ammonia, however, all these substances actually behave as acids. It is significant that those substances listed as analogs of the aquo acids do, in fact, behave as ammono acids in liquid ammonia. It should be emphasized that the true nature of such nitrogen compounds, be they inorganic or organic, actually comes to light when the compounds are dissolved in a solvent to which they are generically related.

OTHER PROTONIC SOLVENT SYSTEMS. There is no question but that the Franklin concept was intriguing. Obviously if nitrogen compounds can be related to ammonia as the parent solvent, why not relate sulfur compounds to hydrogen sulfide? Amines and alcohols are also good solvents. Why cannot these materials serve as parent substances? It should likewise be possible to systematize the chemistry of hydroxylamine and hydrazine derivatives by considering each of the simple compounds as a parent substance. Why should not any protonic solvent, capable of undergoing limited self-ionization into hydrogen ion and some base-analog ion, serve as a parent substance of a system of acids, bases, and salts? Questions such as these led to a tremendous amount of experimental work which showed definitely that it is entirely permissible to set up a generalized solvent theory of acids, bases, and salts. The solvated proton or onium ion may in each case be considered the bearer of acidity. The solvent anion, on the other hand, represents the base-analog ion or group. Some of the solvent systems which have actually been investigated are listed in Table 4. The positive and negative ions presumably formed by the self-ionization of each are also given.

TABLE 4
PROTONIC SOLVENT SYSTEMS

<i>Solvent</i>	<i>Solvated Proton</i>	<i>Base Analog</i>
HX	$\text{HX} \cdot \text{H}^+$	X^-
HOH	H_3O^+	OH^-
HOR	$\text{ROH} \cdot \text{H}^+$	OR^-
HNH_2	NH_4^+	NH_2^-
HNHR	RNH_3^+	NHR^-
HNR_2	R_2NH_2^+	NR_2^-
HN_2H_3	N_2H_5^+	N_2H_3^-
HNHOH	NH_2OH_2^+	NHOH^-
HCONH_2	$\text{HCONH}_2 \cdot \text{H}^+$	HCONH^-
CH_3CONH_2	$\text{CH}_3\text{CONH}_2 \cdot \text{H}^+$	CH_3CONH^-
HSH	$\text{H}_2\text{S} \cdot \text{H}^+$	SH^-
HF	H_2F^+	F^-
$\text{HC}_2\text{H}_3\text{O}_2$	$\text{HC}_2\text{H}_3\text{O}_2 \cdot \text{H}^+$	$\text{C}_2\text{H}_3\text{O}_2^-$

It should be emphasized that experimental evidence shows, in general, that such a point of view does have merit. Hydrazine salts have been found to behave as acids and to react with sodium hydrazide in anhydrous hydrazine to yield salts by a mechanism which is certainly a typical acid-base reaction. Alkoxides, when dissolved in the alcohol as solvent, likewise react with acids in what may be considered to be

typical neutralization reactions. It is significant, however, that the base-analog ion varies with the nature of the solvent, whereas the solvated proton may be formulated in every case as the bearer of acidity.

NON-PROTONIC SYSTEMS OF ACIDS AND BASES. The success which attended the development and extension of the solvent system concept spurred other investigators to consider solvent systems of a non-protonic nature. One of the first of these to be investigated was sulfur dioxide (8). It had already been shown to be an excellent electrolytic solvent and reaction medium, but no particular inclusive point of view had been applied to such miscellaneous observations. Germann (9) extended the solvent theory to non-protonic solvents by demonstrating that typical acid-base reactions can be carried out even in so unfamiliar a liquid medium as phosgene. Typical non-protonic solvents are listed in Table 5; products are also given representing the pre-

TABLE 5
AUTO-IONIZATION OF NON-PROTONIC SOLVENTS

<i>Solvent</i>	<i>Acid Analog</i>	<i>Base Analog</i>
XY	$X(XY)^+$	Y^-
SO ₂	SO^{++}	$SO_3^=$
COCl ₂	$COCl^+$	$COCl_3^-$ or Cl^-
SeOCl ₂	$SeOCl_2 \cdot SeOCl^+$	Cl^-
POCl ₃	$POCl_2^+$ or $POCl_3 \cdot POCl_2^+$	$POCl_4^-$ or Cl^-

sumable auto-ionization of each of them. Not only can base-analog type ions be hypothesized, but positive ions analogous to the hydrogen ion or the solvated proton may also be formulated. Thionyl compounds, for example, can therefore be looked upon as the acids and metal sulfites as the bases, of a sulfur dioxide system. Here again experimental evidence for the usefulness of this point of view was offered, first by Cady (8) and later on a more extensive basis by Jander and his co-workers (10). Thionyl chloride and cesium sulfite do, in fact, react in liquid sulfur dioxide with the formation of cesium chloride in what may be regarded as a typical neutralization reaction.

A very extensive investigation of a non-protonic solvent and of the applicability of the solvent system concept was carried out by G. B. L. Smith (11), using selenium(IV) oxychloride as solvent. His researches cover reactions of metathesis, neutralization, solvolysis, and solvation in selenium(IV) oxychloride and may be considered as classic in so far as extension of the general solvent system concept to non-protonic

solvents is concerned. Nitrosyl chloride (12) has also been investigated from the same point of view.

THE PROTONIC CONCEPT (13)

The original Arrhenius definition limited acids to hydrogen compounds which give hydrogen ion in solution. Bases were in turn characterized by their ability to give hydroxyl ion in solution. Both these characteristic ions were, however, limited specifically to aqueous solution. With the development of the solvent system concept and its application to both protonic and non-protonic solvents, it became apparent that the number of acid-type and base-type ions could be increased almost indefinitely. There was an obvious need for a more unified point of view, and this need was met by both Brönsted and Lowry. In presenting his proposal, Brönsted stated: “. . . if we seek with these considerations as a background (the fact that free hydrogen ions do not exist in solution and that there are many analogs of hydroxyl ions) a more general and a more precise definition of acid and base, we recognize that such a definition must in the first place attribute characteristic acid-base properties to molecules of acids and bases themselves, that is, not to their solutions. Secondly, it must be a definition which relates the ideas of acid and base to each other in a more logical way than has hitherto been the case. It must further give an illuminating explanation of the peculiar character of these substances, and finally we may say that since acids and bases are found so universally in chemical systems, the definitions of these substances must be formulated independently of the solvent” (13).

Both Brönsted and Lowry formulated essentially the same definition. It can be represented by the equilibrium:



In other words, an acid is a molecule or ion which serves as a proton donor; a base is a molecule or ion which acts as a proton acceptor. This definition places in modern terminology the more logical point of view which had been advanced by Gay-Lussac more than a hundred years before in the quotation given on page 24. If the reaction given by the equilibrium above can occur at all, A may be called an acid whatever its charge and B may be called a base irrespective of the actual stoichiometric course of the reaction. If pure hydrogen chloride is an acid, and may under proper conditions release the proton, it is

obvious that the chloride ion is a base (the conjugate base). In the precise application of this definition, it should be pointed out that crystalline potassium hydroxide is an ionic compound, even in the solid state, and should, therefore, more appropriately be called an electrolyte. It consists of two ionic species, only one of which, the hydroxyl ion, is a proton acceptor. In other words, the properties of a base are attributable to the hydroxyl ion rather than to the substance in its formal molecular state.

The protonic definition, however, does imply another consideration. The acid cannot release the proton unless it is brought into contact with some substance which has a higher proton affinity than the conjugate base with which the proton is associated in the original molecule or ion. The definition as implied in the formulation given above involves proton transfer, just as oxidation-reduction reactions involve electron transfer. We may speak of hydrogen chloride as an acid and as a potential proton donor, just as we refer to ferrous ion as a reducing agent and a potential electron donor. Hydroxyl ion is a base because of its high affinity for the proton, just as dichromate ion has the ability to serve as an oxidant or electron acceptor. Reducing agents and oxidizing agents do not behave as electron donors and acceptors, respectively, until they are brought into contact with each other. Dry hydrogen chloride is an acid but does not undergo proton transfer in accordance with the relationship given above until it is brought into contact with a base which is a stronger proton acceptor than the chloride ion.

AQUEOUS SOLUTIONS. Even though the Brönsted definition was formulated "independently of the solvent" it is significant that acids and bases usually do not behave as such until they are brought into a proper medium.

The solvent, therefore, has a profound effect on the development of acidic or basic character. Typical acid-base equilibria in the solvent water are presented in Table 6. Acids release the proton to the water molecules to form the hydrated hydrogen ion, the hydronium ion. An acid may be a molecule such as hydrogen chloride, a cation such as ammonium ion, or an anion such as hydrogen sulfate ion. A base may likewise be a molecule (ammonia), a cation (hydroxo-aquo-ferrous ion), or an anion (acetate or hydroxyl ion).

There is still some dispute as to whether the ions of the solute may formally be regarded as proton donors or proton acceptors or whether the ions formed by reaction of the solute with the solvent represent the reactive species in aqueous solution. It may be assumed, for ex-

TABLE 6

ACID-BASE EQUILIBRIA IN WATER

<i>Acids</i>		<i>Bases</i>		
↓ Acid Character Decreases	$\left\{ \begin{array}{l} \text{HCl} \\ \text{H}_2\text{SO}_4 \\ \text{HSO}_4^- \\ \text{H}_3\text{PO}_4 \\ \text{HC}_2\text{H}_3\text{O}_2 \\ \text{Fe}(\text{H}_2\text{O})_6^{+3} \\ \text{NH}_4^+ \\ \text{H}_2\text{CO}_3 \\ \text{HCN} \\ \text{HCO}_3^- \\ \text{H}_2\text{O} \end{array} \right\}$	$+ \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+$	$\left\{ \begin{array}{l} \text{Cl}^- \\ \text{HSO}_4^- \\ \text{SO}_4^{=} \\ \text{H}_2\text{PO}_4^- \\ \text{C}_2\text{H}_3\text{O}_2^- \\ \text{Fe}(\text{OH})(\text{H}_2\text{O})_5^{++} \\ \text{NH}_3 \\ \text{HCO}_3^- \\ \text{CN}^- \\ \text{CO}_3^{=} \\ \text{OH}^- \end{array} \right\}$	↑ Base Character Decreases

ample, that ammonium ion is a cation acid because it reacts with the solvent water to increase the hydronium ion concentration of the pure solvent water. Yet the ammonium ion is an acid *per se* not only in liquid ammonia, but also in the fused state. In like fashion, it may be assumed that cyanide, acetate, and carbonate ions are bases, since they undergo hydrolysis in water and bring about a decrease in the hydronium ion concentration of the solution. It is equally proper, however, to raise such questions as the following. Do these anions serve as bases "independently of the solvent"? Are there only two ionic types in aqueous solution responsible for acid-base reactions, namely, hydronium ion and hydroxyl ion? This whole matter may be approached in another fashion: Does ammonia accept a proton from hydrogen chloride in aqueous solution by direct reaction "independently of the solvent" or does each of these molecular species first react with the solvent water to give ammonium, hydroxyl, hydronium, and chloride ions which thereupon undergo a typical neutralization reaction involving the disappearance of hydronium and hydroxyl ions?

The authors are inclined to consider questions of this sort irrelevant, but do emphasize the fact that both mechanisms may be applicable. Reactions as they are ordinarily carried out in aqueous solution, or in non-aqueous solvents to which the protonic concept is applicable, take place in relatively dilute solutions. It should, however, be pointed out that many ionic compounds undergo reaction also in the fused state and at higher temperatures, under conditions where to all intents and purposes no "ionizing" solvent is employed, but where the properties of the particular ion *per se* as proton donor or proton acceptor are involved.

THE PROTONIC CONCEPT AND NON-AQUEOUS SOLVENTS. There is no question but that the Brönsted-Lowry definition has helped to elucidate the nature of acid-base equilibria in aqueous solutions. There are obviously many other hydrogen-containing solvents which are capable of undergoing limited auto-ionization to form the solvated proton and the corresponding negative ion which may be looked upon as a solvo base or the conjugate base of the solvent acting as an acid. It becomes apparent immediately that the development of acidic or basic character in non-aqueous solutions depends upon the displacement of the equilibrium which obtains for the parent solvent itself. The generalized protonic theory must explain why urea behaves as an acid when dissolved in liquid ammonia, and why it can be titrated as a base with a solution of perchloric acid in acetic acid. Evidently the solvent exerts a profound effect upon the behavior of the solute.

Reference has already been made in the introductory chapter to the fact that solvents may be classified on the basis of their ability and tendency to coordinate the proton, that is, their apparent tendency to serve as proton acceptors. Review and amplification of this classification (14) would seem desirable at this point, since the extension of the protonic concept to non-aqueous solvents depends upon solvent character.

1. Basic solvents such as ammonia and the amines coordinate the proton strongly, and will therefore convert many hydrogen compounds into the corresponding onium salts. The acidic character of hydrogen compounds dissolved in basic solvents is thereby enhanced. The degree of dissociation of the resulting electrolyte, however, is quite another matter, and will generally be lower than in water since none of the common non-aqueous solvents has as high a dielectric constant as water.

2. Acidic solvents, such as acetic acid, sulfuric acid, and hydrogen fluoride, are usually poor proton acceptors. They are better proton donors, and convert weak bases into the corresponding onium salts; an increase in the concentration of the base-analog ion of the solvent is thereby brought about. Again, the basic character of a substance may be enhanced by solution in an acidic solvent.

3. Amphiprotic solvents occupy a position intermediate between those of marked protophylic character, such as ammonia and the amines, and those of distinct protophobic character, such as acetic acid and hydrogen fluoride. Water and most of the hydroxylic solvents may be placed in this category. Water as a solvent releases the proton to those substances which are proton acceptors, but it also has

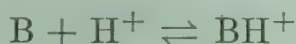
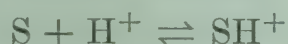
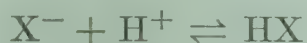
the ability to coordinate hydrogen ion to form the hydronium ion and, in the latter respect, it resembles the more basic solvents.

4. The aprotic solvents include media where little or no proton exchange between solvent and solute can take place. Manifestation of acidic character in these solvents depends on the tendency of the solute molecule to release the proton to other solutes which are capable of acting as bases. Aprotic or inert solvents are differentiating in character, that is, the intrinsic acidity of the solute is revealed in such media. The hydrocarbons, both aliphatic and aromatic, as well as chlorinated and halogenated organic compounds are the commonest and the most widely used aprotic solvents.

Since solvents vary so widely in their ability to serve as proton acceptors, the nature of the solvent will greatly affect the behavior of a dissolved solute. Thus, substances like arsine, phosphine, urea, acetamide, and even the aromatic amines act as acids in liquid ammonia. In water, these substances are either inert or very weakly basic. Some of these same compounds actually behave as bases when dissolved in acidic solvents. This is specifically true of urea and acetamide in acetic acid. Even nitric acid, which is a strong acid in aqueous solution, becomes a proton acceptor, that is a base, when dissolved in anhydrous hydrogen fluoride. Actually there are very few, if any, solutes which are capable of serving as Brönsted acids in anhydrous hydrogen fluoride for the simple reason that practically none of the common strong acids is capable of releasing the proton to a greater extent than the solvent itself. Potassium acid phthalate is an acidimetric standard in water, but actually serves as a base standard in glacial acetic acid.

Acidic solvents are interesting from another point of view, since it is in these solvents that differentiation in acid strength occurs. This has been shown to be the case especially in such a useful solvent as acetic acid. Perchloric acid is apparently the strongest acid in acetic acid (or, for that matter, in any solvent) and is a much stronger acid than sulfuric acid, or hydrogen chloride. Such facts must be borne in mind when acid types are dissolved in highly acidic solvents. The mere fact that certain acids are all uniformly strong in aqueous solutions is no criterion that the same equivalence of acid strength will be retained in non-aqueous solutions. Still, the tendency for the molecule of the acid to release the proton is often most conveniently demonstrated in a completely inert solvent. This effect has been evaluated by Hantzsch and others through a study of indicator reactions with various acids in inert solvents, such as chloroform and ether.

SALT FORMATION (15). Development of acid or base character and salt formation depend on a number of competing equilibria which may be represented by the following equations:



where HX is the substance which acts as an acid in the solvent, S is the solvent, and B is the substance which acts as a base in the solvent.

The tendency for a hydrogen compound to act as an acid depends first of all on the nature of the molecule or ion itself, that is, upon the so-called intrinsic acidity. This is determined by the tendency on the part of the anion to release the proton; it decreases with increasing tendency for the conjugate base to attract the proton. For oxyacids, the charge and size of the acid-forming element are important. Perchloric acid is thus a stronger acid than sulfuric acid or phosphoric acid under all conditions. However, a proton donor will act as an acid toward a given solvent only if there is some tendency on the part of the solvent to form the onium ion. The basicity of the solvent, that is, its tendency to form a stable onium ion, is a factor which determines whether or not the acid character of a solute is developed with respect to the solvent. The third of the above equilibria indicates that the base will also be competing with the solvent and the acid anion for the proton. A substance will not act as a base unless it has a higher affinity for the proton than the solvent or the acid anion.

The reaction of salt formation in solvents may, therefore, be represented by the following equation:



Salt formation in solvents will, therefore, not take place unless the base has a higher affinity for the proton than the solvent has. Thus salts of weak acids are often obtainable in solvents such as liquid ammonia, the amines, and pyridine. Salts of weak bases can in like manner often be obtained by reaction with a strong acid in acetic acid. Since acetic acid is a differentiating solvent, it would seem logical, however, to employ solutions of perchloric acid in acetic acid for the titration of weak bases and for the preparation of salts.

LIMITATIONS OF THE BRÖNSTED-LOWRY DEFINITION. The protonic concept is specifically limited to hydrogen-containing solvents. Pro-

ton transfer becomes the important process. Actually, according to this concept, neutralization is not considered to be the essential criterion for an acid-base reaction. Salt formation is purely incidental to the reaction between acids and bases in various non-aqueous media. The protonic theory, furthermore, does not take into account the many possible non-protonic solvents in which acid-base type reactions have been shown to occur even though no proton transfer is involved. Some of the objectors to the Brönsted definition have actually gone so far as to refer to the adherents of the concept as the "cult of the proton." Such ridicule is not justified, since there is no question but that the protonic theory has been extremely useful in spite of its shortcomings. The protonic concept did place emphasis for the first time upon the definition of acids and bases from a simple and unified point of view. Second, it did relate development of acidic or basic character to the solvent even though definitions were formulated independently of the solvent; and third, even though salt formation was not considered to be a primary criterion, it did indicate in a practical way how the proper solvent might be chosen in order to facilitate salt formation.

THE ELECTRONIC THEORY (16)

Development of the electronic theory of the structure of matter made it possible to establish a still more general concept of acids and bases. This theory was first promulgated by G. N. Lewis (4) and, like the Brönsted-Lowry concept, defines an acid in terms of opposite-ness in character to a base. According to the electronic theory an acid is an electron pair acceptor; a base is an electron pair donor. An acid is coordinatively unsaturated and will accept a share in an electron pair with the resultant formation of a coordinate covalent bond. Ionization of the product may follow. Neutralization involves initial formation of a covalent bond. Every reaction involving coordination, whether it involves the formation of a complex ion or a covalent molecule, may therefore be labeled an acid-base reaction!

In Table 7 are presented examples of typical bases and acids. Formulas for the neutralization products of acid-base pairs are also listed. Triethylamine, for instance, is a base from the Brönsted point of view. It is also an electron pair donor. Boron trichloride, on the other hand, is electron-deficient and will, therefore, share an electron pair offered to it by the triethylamine molecule to form a molecular covalent compound. Formation of a covalent compound between an ether and sulfur trioxide is also an example of neutralization, the

TABLE 7

THE ELECTRONIC THEORY OF ACIDS AND BASES

<i>Bases</i>	<i>Acids</i>	<i>Neutralization Product</i>
R_3N	BCl_3	$R_3N \cdot BCl_3$
R_2O	SO_3	$R_2O \cdot SO_3$
R_3N	HCl	$R_3N \cdot HCl \rightarrow R_3NH^+ + Cl^-$
H_2O	HCl	$H_2O \cdot HCl \rightarrow H_3O^+ + Cl^-$
$COCl_2$	$AlCl_3$	$COCl_2 \cdot AlCl_3 \rightarrow COCl^+ + AlCl_4^-$
HCl	$SnCl_4$	$SnCl_4 \cdot 2HCl$
NH_3	H^+	NH_4^+
NH_3	Ag^+	$Ag(NH_3)_2^+$
Cl^- } NH_3 }	Co^{+3}	$Co(NH_3)_4Cl_2^+$

ether being the electron pair donor and, therefore, the base. When the reaction between triethylamine and hydrogen chloride occurs in a solvent such as benzene, the corresponding onium salt is precipitated from solution. The covalent bond is actually formed between the proton and the tertiary amine. This step is undoubtedly, however, preceded by the formation of a hydrogen bond between tertiary amine and hydrogen chloride, followed by transfer of the proton to the stronger base. Interaction of hydrogen chloride with water may likewise involve intermediate formation of a hydrogen bond and subsequent transfer of the proton to form the hydronium ion. Germann found that the solvent carbonyl chloride dissolves aluminum chloride, and that the resulting solution has all the properties of an acid. In this case the solvent carbonyl chloride is the base; aluminum chloride, being electron deficient, is the acid. Some sort of a covalent compound is formed initially, but the end result is the formation of a complex chloraluminum ion to which may be assigned the formula $AlCl_4^-$.

According to the electronic concept, so ably presented by Luder and Zuffanti (16), all cases of coordination may be considered acid-base reactions. Coordination is involved when ammonia gas is passed into an aqueous solution of an acid. Here the proton may be considered to be solvated, as are all other ions in aqueous solution. Nevertheless, the reaction may be represented most simply by the process of attachment of the electron-deficient proton to the ammonia molecule to form the ammonium ion. Whereas coordination of the proton, because of its small size, is generally considered to be a distinctive process, it is fundamentally no different from the process which results in the formation of any other complex ion. The reaction between silver ion in aqueous solution and ammonia molecules to form the

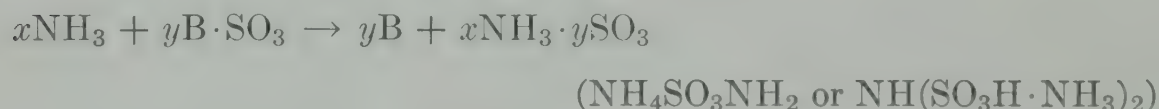
complex diammine silver(I) ion is, therefore, a typical acid-base reaction. In this case, the reaction actually involves displacement of molecules of water of solvation by the more basic ammonia molecules. The formation of the dichlorotetramminecobalt(III) ion, as depicted by the last example, represents an acid-base reaction in which both chloride ions and the ammonia molecules, acting as bases (electron pair donors), satisfy the electron deficiency of a trivalent cobalt ion.

EXPERIMENTAL CRITERIA. Certain experimental criteria have been set up as characteristic of acids and bases:

1. *Neutralization.* This is again the important criterion. The formation of a covalent compound is assumed to be the primary process; this may be followed by ionization.

2. *Indicator reactions.* These do not necessarily depend upon the presence of hydrogen ion. For example, crystal violet is yellow in acid and violet in basic solution; pyridine both in water and in chlorobenzene gives the violet color. Boron trichloride and stannic chloride, when added to pyridine in chlorobenzene, cause the color to change to yellow.

3. *Displacement reactions.* An acid or base will displace a weaker acid or base from its compounds. Reference has already been made to the fact that ammonia displaces water from solvated hydrogen or silver ion. Ammonia is, therefore, a stronger base than water. The reactions of liquid ammonia with sulfur trioxide addition compounds further illustrate such displacement reactions:



The weaker the bond between sulfur trioxide and the donor base in the compound $y\text{B} \cdot \text{SO}_3$, the more violent is the reaction with liquid ammonia and the smaller is the proportion of ammonium sulfamate in the reaction product. These reactions have been used to set up a qualitative sequence of base strength, as shown in the following series:



All the compounds listed in this series are substances which form complexes with sulfur trioxide.

4. *Catalytic activity.* The most useful application of the Lewis theory is to be found in the interpretation of the catalytic activity of non-hydrogen-containing substances. Substances like ammonium chloride, hydrogen ion, sulfur trioxide, boron trifluoride, and iron(III)

bromide are all acid catalysts and may in many instances be used interchangeably. Many examples of such acid- and base-catalyzed reactions in the field of organic chemistry are given by Luder and Zuffanti. There is no question but that the organic chemist is finding such a point of view of real value.

The Lewis concept is certainly the most fundamental and inclusive proposal that has ever been presented. Like many of our older concepts, however, it is in danger of being extended to cover altogether too many phenomena—to which, incidentally, it was never intended to apply. Even oxidation-reduction reactions are considered by some of its proponents to represent a phase of acid-base behavior. Interesting as such extensions may be, they nevertheless confuse the issue and are of limited value. Like the solvent system and the protonic concepts, the Lewis definition is a useful idea and one which has been demonstrated to have utility in both inorganic and organic synthetic chemistry.

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LIQUID AMMONIA AS A SOLVENT AND DISPERSION MEDIUM

It is doubtful if such rapid strides could have been made in the field of non-aqueous solvent chemistry had it not been for the experimental skill, the vision, and the imagination of Edward Curtis Franklin, Charles A. Kraus, and Hamilton P. Cady (1). Their early work with liquid ammonia as a solvent and reaction medium, begun in the late nineties, must be regarded as outstanding in its influence upon the development of chemical science during the first fifty years of the twentieth century. It is true that sporadic attempts had been made prior to 1900 to study reactions and solubility relationships in ammonia. Important among these early efforts were the investigations of Weyl, of Seely, of Gore, and especially those published by Joannis. It is to be regretted that the work of the French investigator Joannis (between 1890 and 1894) did not achieve wider recognition. Many of the reactions first observed qualitatively by Joannis were rediscovered years later by investigators who were completely unaware of the existence of the early French work. This does not detract in the least, however, from the accomplishments of Franklin and of Kraus. They initiated and then continued for many years their experimental efforts in the field of liquid ammonia chemistry. Their results attracted the attention of many other scientists, with the result that a school of "liquid ammonia" chemists, most of whom were students of either Franklin or Kraus, came into existence. The Franklin group became interested primarily in descriptive organic and inorganic chemistry as related to reactions in liquid ammonia; Kraus and his students devoted themselves principally to the physicochemical aspects of solutions in liquid ammonia. Still others like A. W. Browne made use of liquid ammonia as a solvent, even though they were primarily interested in the field of nitrogen chemistry.

It is difficult to analyze in retrospect the motivating factors which caused Franklin and Kraus to undertake their work with ammonia.

It had apparently long been recognized that derivatives of water have their analogs among certain ammonia derivatives; it remained for Franklin and Kraus (2) to point out, however, "that the intimate relationship existing between the two liquids seems to have never been fully recognized." To quote further from this same article:

"Of all known liquids, ammonia most closely approaches water in all those properties which give to water its conspicuous position among solvents. In its capacity as a general solvent for salts it is secondary to water, but superior to all other solvents. It closely approaches water in its power of dissociating electrolytes; some salts conduct electricity even better in ammonia solution than they do in water solution. It plays a part in many compounds analogous to that occupied by water in salts containing water of crystallization. Its heat of volatilization and probably its association constant are higher than those of any other liquid with the one exception of water. For a substance of such simple composition its critical temperature and critical pressure, and even its boiling point at atmospheric pressure, are remarkably high, as is still more conspicuously true of the corresponding constants in the case of water. Its specific heat is quite as great as that of water while its molecular elevation constant is lower than that of any other substance for which measurements have as yet been made.

"Ammonia differs from water in its inability to dissolve the sulfates and sulfites, the alkaline carbonates, phosphates, and oxalates, the hydroxides of the alkali and alkaline earth metals, and the facility with which it dissolves many organic substances, in which latter respect it reminds one of alcohol rather than of water. The liquid does not exhibit a maximum density above the freezing point nor is the solid ammonia specifically lighter than the liquid at its freezing point, as is true of solid and liquid water."

The properties of ammonia and of water are summarized in Table 8. A casual comparison would hardly lead to the conclusion that these two substances are, in fact, quite similar. That they are very much alike becomes more readily apparent from a consideration of the fact that both ammonia and water occupy anomalous positions among the hydrides of their respective periodic groups. Liquid ammonia is characterized by properties which are out of line when compared with those of phosphine, arsine, stibine, and the hypothetical bismuth hydride. In like fashion, water is certainly very different in its chemical and physical properties from the related hydrides of the sixth group of the periodic system. The anomalous character of both ammonia and water is due to the fact that each is an associated solvent; in neither case

TABLE 8

PHYSICAL CONSTANTS OF AMMONIA AND OF WATER

	<i>Ammonia</i>	<i>Water</i>
Boiling point, °C.	-33.35	100
Freezing point, °C.	-77.7	0
Density, g./cc.	0.65 (-10°)	1.00 (4°)
Critical temperature, °C.	132	374
Critical pressure, atm.	112	218
Specific heat, cal./g.	1.10 (0°)	1.00 (20°)
Heat of vaporization, cal./g.	327 (-33°)	541 (100°)
Heat of fusion, cal./g.	83.9 (-77°)	79.7 (0°)
Dielectric constant	22 (-33°)	81.7 (18°)
Specific conductance	5×10^{-11} (-33°)	4×10^{-8} (18°)

does the liquid consist of simple molecules, but rather of more complex aggregates. The abnormally high melting and boiling points, the high dielectric constants, and the high heats of vaporization and fusion of each of these substances may be cited as evidence for such association. Both these substances, from the older point of view, may be looked upon as excellent ionizing solvents.

Ammonia is an excellent solvent for the many nitrogen compounds which are related to it as the parent substance in much the same way that oxygen compounds are related to water. The solvent system concept, with specific reference to ammonia, is taken up in detail in Chapter 4 and must be borne in mind throughout the entire discussion of reactions in ammonia. Whereas ammonia does dissolve many inorganic compounds, it is not as satisfactory a solvent for ionic compounds as water; what it lacks with respect to inorganic compounds it makes up in its solvent ability for organic compounds, especially organic nitrogen compounds.

Liquid ammonia is also an excellent electrolytic solvent. Because ammonia is a more fluid medium than water ionic mobilities are higher in liquid ammonia than in water. Conductance values for typical electrolytes are higher than for the same substances in aqueous solutions.

In view of the fact that ammonia is a typical ionizing solvent, it is not at all surprising that many different types of reactions can be carried out in liquid ammonia. Reactions of metathesis, of solvolysis and solvation, more specifically designated as ammonolytic and ammonation reactions, are reviewed in Chapter 5. Ammonolytic reactions bring about a change in the nature of the dissolved solute, and also increase the concentration of either the ammonium or amide ions.

The high solubility of the alkali and alkaline earth metals, the physical properties of such solutions and their use as powerful reducing agents single out such systems for special emphasis. The reactions which these solutions undergo are among the most unusual reactions to be found in the whole realm of chemistry. Reactions of such metal-ammonia solutions with both inorganic and organic compounds are taken up in Chapter 6.

Thirty years ago chemists might have looked upon the idea of reactions in liquid ammonia with some misgivings. Today, however, the use of ammonia as a solvent offers no experimental difficulties whatsoever, with the result that it is used widely in both organic and inorganic synthetic chemistry. Ammonia is obtainable as the synthetic anhydrous product in substantial quantities and at a reasonable price. Actually, there are few anhydrous solvents, either inorganic or organic, which can compete with liquid ammonia as a solvent on the basis of cost. Certainly this is one factor which should even today warrant the wider practical use of ammonia as a solvent.

SOLUBILITIES IN LIQUID AMMONIA

Weyl (3), Seely (4), and Gore (5) were among the early investigators to record solubilities of various substances in liquid ammonia. The first extensive investigation, however, was carried out by Franklin and Kraus (2), who undertook to provide semi-quantitative information concerning the solubilities of some 500 different substances. Fortunately, there are available several excellent reference sources (6, 7, 8, 9, 10) which may be consulted for information on qualitative and quantitative solubilities of both inorganic and organic substances. General trends are reviewed in the following section.

ELEMENTS. The alkali and alkaline earth metals dissolve in ammonia to give a characteristic deep blue solution. Evaporation of such solutions with removal of ammonia permits recovery of the less active alkali metals. Evaporation of solutions of the alkaline earth metals, on the other hand, leads to formation of very unusual salt-like metal ammines with the type formula $M(\text{NH}_3)_6$. Quantitative solubility data for the alkali metals in liquid ammonia are summarized in Table 9. These values are extraordinarily high when compared with data for such readily soluble substances as sodium chloride and sodium sulfate in water (35.9 and 11.1 grams per 100 grams of water at 18°, respectively).

The stability of solutions of the alkali and alkaline earth metals in liquid ammonia decreases with increasing atomic weight. Solutions

TABLE 9
SOLUBILITY OF ALKALI METALS IN LIQUID AMMONIA

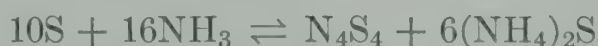
<i>Metal</i>	<i>Temperature</i>	<i>Grams/100 g. NH₃</i>
Lithium	-63.5°	10.698
	-33.2°	10.866
	0°	11.319
Sodium	-33°	24.6
Potassium	-33°	49.0

of sodium are stable for months; cesium solutions deteriorate quite rapidly. Reaction takes place with formation of the amide and evolution of hydrogen gas in accordance with the general equation:



In view of the distinctive character of such metal-ammonia solutions and their wide use in reduction and in synthetic organic and inorganic reactions, further and more complete discussion of the nature and properties of these systems is taken up in Chapter 6.*

Iodine, phosphorus, and sulfur are also soluble; it is claimed that some solubility is exhibited by selenium. In all these instances, solution involves reaction between solvent and solute. More extensive investigation of the solubility behavior of these substances is certainly in order, together with more definite information concerning the particular allotropic modification for which solubility is claimed. It has been proved definitely that the solution process for sulfur can be represented by the equilibrium



Fresh solutions of sulfur in liquid ammonia can be evaporated to reform elemental sulfur, but the modification of sulfur obtained under these conditions is not specified. Removal of the sulfide ion can also be accomplished to shift the equilibrium to the right, with formation of tetranitrogen tetrasulfide.

* It is also possible to obtain solutions of magnesium and aluminum in liquid ammonia; they impart the characteristic blue color to the solvent. It may be anticipated that the more active metals of the third group, specifically the rare earths, will also yield such deep blue solutions in liquid ammonia. It is probable that these can also be made by procedures similar to those which led to the preparation of a solution of metallic aluminum, that is, by careful electrolysis of the appropriate metallic anode in a liquid ammonia solution of a salt of the metal (11).

INORGANIC COMPOUNDS. Those metallic salts which are most highly solvated (and usually most difficult to prepare in the anhydrous state) usually exhibit highest solubilities, not only in liquid ammonia but also in other non-aqueous solvents. The nature of the anion thus influences markedly solubility in liquid ammonia. Thiocyanates, perchlorates, nitrates, nitrites, and persulfates tend to be the more soluble salt types. Iodides are more soluble than the bromides and the chlorides. Most fluorides are insoluble in liquid ammonia. Iodides are more highly polarized and more covalent in character than bromides, chlorides, and fluorides, in the given order. Solution of iodides is thus accompanied by extensive solvation, which is greater the smaller the cation and the higher its charge. Although substances which tend to solvate generally exhibit greatest solubility in non-aqueous solvents, there are exceptions. Both calcium and zinc chlorides are extremely soluble in water, but practically insoluble in liquid ammonia. When brought into contact with ammonia at $-33^{\circ}\text{C}.$, these substances undergo a slaking process and are converted into the 8- and 10-ammoniates, respectively. Ammonium sulfate is also insoluble in ammonia, but reacts to form the 3-ammoniate, which is stable at $-33^{\circ}\text{C}.$

Both red mercuric iodide and yellow lead iodide are very soluble in ammonia to yield colorless solutions from which the 2-ammoniates may be crystallized upon concentration. Sodium chloride forms a 5-ammoniate which is stable below $-9.5^{\circ}\text{C}.$ (2.767 atm. pressure). Copper, nickel, and cobalt salts give solutions (or are converted into insoluble products) possessing the characteristic colors of the metal ammine ions developed in aqueous solutions containing excess ammonia. The process of ammoniation is therefore concomitant with the process of solution.

Oxy acid salts, such as the sulfates, sulfites, carbonates, phosphates and arsenates, and oxides, hydroxides, and sulfides, are generally insoluble in ammonia.

Most ammonium salts with the exception of the oxy acid salts mentioned above are soluble and act as acids in liquid ammonia. Some ammonium salts, such as the nitrate, the thiocyanate, and the acetate, are extremely soluble in ammonia. These substances are "ammonodeliquescent," for they take up sufficient ammonia gas even at $0^{\circ}\text{C}.$ to form solutions whose ammonia vapor pressure is reduced to such an extent that solutions are stable at that temperature. Especially characteristic in this respect is the saturated solution of ammonium nitrate in liquid ammonia which can exist even up to room temperature and which is sometimes known as Divers' solution, after the English chemist who first investigated its behavior.

A representative listing of solubilities of inorganic compounds in liquid ammonia where quantitative data have been recorded is given in Table 10. Experimental methods which may be used to determine

TABLE 10

SOLUBILITIES OF SOME INORGANIC SALTS IN LIQUID AMMONIA AT 0°C. IN GRAMS/100 G. SOLUTION

[According to Linhard and Stephan (12)]

<i>Metal Ion</i>	<i>Anion</i>			
	Cl	Br	I	NO ₃
Li	1.43
Na	11.37	39.00	56.88	56.05
K	0.132	21.18	64.81	9.52
Rb	0.289	18.23	68.15
Cs	0.381	4.38	60.28
Ag	0.280	2.35	84.15
NH ₄	39.91	57.96	76.99
Mg	0.004	0.156
Ca	0.009	3.85	45.13
Sr	0.008	0.308	28.77
Ba	0.017	0.231	17.88

quantitative solubilities in liquid ammonia and in other liquefied gases have been described by Linhard and Stephan (12), Hunt (13), Johnson (14), Watt (15), and others (16, 17).

ORGANIC COMPOUNDS. The less polar nature of ammonia and the fact that it is not as highly associated probably account in part for the observation that organic compounds are more readily soluble and dispersible in ammonia than they are in water. Ammonia is a somewhat better hydrogen bonding agent than water since there is less attraction of solvent molecules for each other. The higher basicity of ammonia as a solvent also comes into play, with the result that chemical character of solutes is thereby often changed completely. Solubility of any particular class of organic compounds generally decreases as the size of the attached carbon radical becomes larger.

Most of the simple saturated aliphatic hydrocarbons are insoluble in boiling liquid ammonia and at room temperatures. Olefins and the acetylenes are more soluble, possibly because these unsaturated hydrocarbons are more acidic in character. Among the aromatic hydrocarbons, benzene is freely soluble even at the boiling point of liquid ammonia, whereas toluene forms two liquid phases at lower temperatures with an upper critical solution temperature of approximately 15°C.

Alcohols and phenols are potential proton donors in the solvent liquid ammonia. The simple alcohols are miscible in all proportions. Polyhydric alcohols, such as ethylene glycol and glycerol, are extremely soluble. The monohydric phenols and related polyhydroxy derivatives are also quite soluble.

Diethyl ether is moderately soluble, but higher ethers with larger organic radicals become less and less soluble. Simple esters, such as diethyl carbonate, ethyl acetate, ethyl and methyl benzoate, are miscible in all proportions. The methyl, ethyl, and possibly the propyl esters of the simple carboxylic acids are generally miscible with ammonia, but solubility decreases very markedly as the alkyl groups increase in size. Depending upon the activity of the alkyl radical, esters tend to react with the solvent to form the corresponding alcohols and the acid amides. (See ammonolytic reactions.) Simple aldehydes and ketones, both aliphatic and aromatic, appear to be fairly soluble in liquid ammonia; aldehydes, however, react to a considerable extent.

The alkyl sulfuric acids and many alkyl and aryl sulfonic acids are converted into the ammonium salts and are fairly soluble in ammonia, in contrast to the behavior of sulfuric acid. This difference in solubility has afforded a very convenient means for separation of sulfonation and sulfation products of organic compounds from excess sulfuric acid (18).

Carboxylic acids are converted into the corresponding ammonium salts. Those of low molecular weight are soluble. The more complex fatty acids, especially those of higher molecular weight, become correspondingly less soluble. Stearic acid is readily converted by reaction with liquid ammonia into the ammonium salt and is sufficiently soluble so that the surface tension of the resulting liquid ammonia solution is considerably decreased. Rosin (abietic acid) is not soluble, but undergoes reaction with conversion to the ammonium salt.

NITROGEN COMPOUNDS. It is with respect to nitrogen compounds, especially those designated as ammono compounds, that liquid ammonia finds its greatest usefulness, not only because these substances are related generically to ammonia as the parent substance, but also because the factor of chemical similarity helps in the solution process. Nitrogen compounds are generally more soluble in liquid ammonia than in any other solvent.

The amines represent the alcohol analogs with respect to ammonia as the parent substance. The simple amines are quite soluble. It is

interesting to note that a certain parallelism exists between the solubilities of alcohols in water on the one hand, and those of the amines in ammonia on the other. Solubility decreases as the molecular weight and the degree of substitution in the amine molecule increase. Triethylamine is said to be only partly miscible with ammonia at 0°C ., but completely soluble in all proportions at 20°C . Hexylamine separates into two layers at -33°C ., but it is completely miscible with ammonia at higher temperatures.*

The acid amides and the amidines representing the nitrogen analogs of the carboxylic acids are also rather soluble in liquid ammonia. Here again solubility decreases as the attached organic radicals become larger. Compounds like acetamide, benzamide, and acetamidine are very soluble in liquid ammonia.

Heterocyclic nitrogen compounds such as pyridine, quinoline, indole, pyrrole, and carbazole have all been found to be soluble in liquid ammonia. Recent work has also indicated that such classes of materials as the simple triazoles, tetrazoles, and triazines exhibit greater solubility in ammonia than in aqueous solution. Here again, similarity in chemical character and the fact that these substances are nitrogen compounds are in a large measure responsible for their solubility.

Other classes of nitrogen compounds exhibit unusual solubilities. Such substances as hydrazine and hydroxylamine are very soluble in liquid ammonia and can be recovered unchanged after evaporation of the solvent. Most unusual, however, is the solubility of both aliphatic and aromatic nitro compounds in liquid ammonia. The resulting solutions are still more striking since these substances, which normally can be considered as non-electrolytes, give evidence of having undergone reaction with the solvent, with the formation of highly conducting solutions. Solutions of the aromatic nitro compounds are also highly colored.

Liquid ammonia has been recommended as a preferential solvent for the extraction of alkaloids and sugars from natural products, for the removal of phenols from coal tars, and the purification of, and the removal of sulfur compounds from, petroleum products. Suggested technical applications are covered by an extensive and ever-growing list of American and foreign patents.

* It is to be regretted that so little work has been published dealing with critical phenomena involving liquid ammonia. Certainly a fundamental investigation of this sort might reveal some interesting possible uses for liquid ammonia as an extractive solvent, especially for organic compounds.

COLLOIDAL PHENOMENA IN LIQUID AMMONIA

Little published work is available on the behavior of liquid ammonia as either a lyophilic or a lyophobic dispersion medium. Papers by Taft (19, 20, 21) and a few others represent the total source material covering this extremely interesting, and possibly very important, subject. Such colloidal systems in liquid ammonia may be appropriately designated as ammonosols to differentiate them from the aquosols, in which water is the dispersion medium, and from the organosols, in which an organic liquid is the continuous phase.

Taft studied qualitatively the dispersibility of a large number of substances in liquid ammonia, both at the boiling point of the solvent and at room temperature. He investigated specifically those substances which were known to yield colloidal dispersions in other solvent systems. Detailed observations are listed by Taft (19, 20) in his original papers; generalizations with respect to various classes of materials follow.

CARBOHYDRATES AND RELATED COMPOUNDS. Ammonia at its boiling point takes into solution cellulose acetate, dextrin, inulin, glycogen, and the nitro-cottons. Except for glycogen, dispersibility increases with rise in temperature. Rise in temperature causes the glycogen to precipitate, but lowering the temperature causes the product to redissolve. Dextrin shows normal solubility behavior, being more soluble at higher temperatures; the excess solute precipitates from solution upon cooling. These processes are reversible for both glycogen and dextrin. Whereas the cellulose acetates and nitrates definitely form colloidal dispersions it was observed that no reversibility characterizes such systems. Instead, cellulose acetate dispersions were found on standing to set to thick gels. Such gelation reactions occur more rapidly at higher temperatures and also in the presence of water. Dispersions of cellulose nitrates give evidence of chemical change since they become progressively darker in color with age.

PROTEINS AND RELATED COMPOUNDS. Only zein, nucleinic acid, proteose peptone, and bacto-peptone were observed to disperse markedly. Gliadin is more dispersible at low temperature and precipitates on warming. Here again this process is reversible even after such solutions have stood for several days. The solid precipitating at room temperature becomes blue, but this color disappears after several days.

MISCELLANEOUS SUBSTANCES. Dyes display some solubility, giving characteristic color reactions. Gums and resins appear to be non-dispersible although reference is made to the swelling action of ammonia

on a number of phenol-formaldehyde resins. Soaps are likewise listed as non-dispersible. Taft (20) does suggest that "peptizing agents or methods could be found" to effect dispersion and that "acidic or alkaline reagents in liquid ammonia be tried." The possibility of "using this solvent [ammonia] as a means of purification or separation where dispersion [solution] occurs" is also emphasized with particular reference to the cellulose esters, zein, and gliadin.

A more extended study was made subsequently of the dispersibility of cellulose acetate (21) in liquid ammonia. Ammonosols from very dilute solutions to ones containing 60 grams per 100 cc. of ammonia were prepared successfully, although products containing high concentrations were very viscous and difficult to handle. Sols containing 1% cellulose acetate were clear, colorless mobile liquids at first, but became more viscous on aging, especially at room temperature. Such dispersions eventually set up to thick gels, the rate of gel formation increasing with temperature and with concentration. A dispersion containing 5% cellulose acetate (degree of acetylation not specified) was found to gel completely in 18 hours at 25°C., in 60 hours at 0°, but required 21 days at -33°C. Presence of water was found to accelerate gel formation, especially in the case of dilute dispersions, the addition of 5% water speeding up the time of gelation for a 0.5% dispersion from 38 to 20 hours. Such cellulose acetate dispersions were studied later by Audrieth and Campbell (22). Gelation was found to be due to ammonolysis, with formation of acetamide and a regenerated type cellulose giving the characteristic x-ray diffraction pattern of such a product.

Ammonia is absorbed by cellulose to yield an ammoniated cellulose which is unstable at higher temperatures. It is claimed that the physical properties of regenerated cellulose (such as cellophane film) (23) are markedly changed by the action of liquid ammonia to greatly increase tear strength, tensile strength, thickness and weight per unit area, with a corresponding decrease in length and width of samples. Bags of regenerated cellulose film may be used to effect dialysis of ammonia solutions.

Liquid ammonia solutions of ammonium thiocyanate, sodium iodide, sodium thiocyanate, and sodium nitrate dissolve both regenerated and cotton cellulose to give clear solutions, from which the cellulose can be precipitated in a flocculent condition by dilution with water. The information given originally was, however, subjected to further study subsequently, indicating that presence of water has an important effect on such dispersion reactions. Only sodium and ammonium thiocyanates can disperse both materials in absolutely an-

hydrous ammonia, whereas the other two salts were found to dissolve only the regenerated cellulose. Taft had previously shown that filter paper could be dispersed to form a stiff gel in saturated solutions of lithium iodide and of barium thiocyanate, both of which are extremely soluble in ammonia.

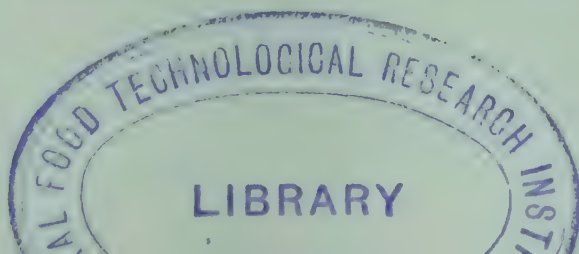
Qualitative experimental observations also show that the Hofmeister series holds for dispersions in ammonia (19). The influence of the anion in facilitating dispersion of pyroxylin in salt solutions (approximately 1 *M* or saturated) is given by the following order: NaCl, NaNO₃, NaC₂H₃O₂, pure ammonia, NaI, and NaSCN. The thiocyanate solution is the most effective dispersion medium.

The behavior of inulin deserves further comment. Earlier work had indicated that this sugar dissolves in ammonia as a difructose, in which event it should dialyze as easily as sucrose since both are of the same molecular magnitude. Dialysis experiments using a cellophane membrane proved conclusively that no inulin passed through the membrane, but that sucrose did so readily (24). The colloidal nature of the inulin dispersions was further substantiated by the fact that such solutions give a pronounced Tyndall effect, whereas solutions of sucrose and lactose are optically clear. Extraction of inulin from dried Jerusalem artichokes is possible, but the product recovered in this manner leaves a glassy mass on evaporation of the solvent (25).

Liquid ammonia has been covered patent-wise for the treatment and purification of cellulose esters and for extraction of ergot and other naturally occurring products which may conceivably be taken into colloidal dispersion.

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THE NITROGEN SYSTEM OF COMPOUNDS

Brief reference was made in connection with the discussion of acidic and basic behavior in non-aqueous solvents to the general utility of the solvent system concept. It was pointed out that formal relationships to be gleaned from such a concept can be established for many systems of compounds; but in no instance has this concept been developed and applied more successfully than in the case of nitrogen compounds in their relationship to ammonia as the parent solvent. The solvent system concept was developed when it was recognized that nitrogen compounds behave in ammonia as the solvent in a manner quite similar to that of analogous oxygen compounds in aqueous solution. Not only has this idea been helpful in systematizing and classifying the chemistry of nitrogen compounds, but the concept has become through the years a very useful working hypothesis. It has been subjected to extensive experimental verification by a study of reactions in liquid ammonia as the solvent. Further discussion of some of these relationships is therefore justified, since a clear understanding thereof is essential to the successful use of ammonia as a reaction medium.

The auto-ionization of ammonia to give ammonium and amide ions takes place as follows:



This equilibrium immediately specifies the acid and base analogs in ammonia as the solvent. Ammonium salts, which already have the preformed ammonium ion in the crystal lattice, dissolve in liquid ammonia to produce acidic solutions. All substances which undergo solvolysis, specifically ammonolysis, to bring about an increase in the ammonium ion concentration also yield acidic solutions. This is particularly true of covalent compounds of the non-metals with halogen,

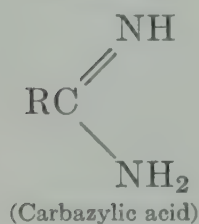
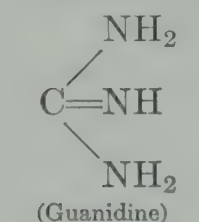
sulfur, and even oxygen, such as sulfuryl chloride, phosphorus(V) sulfide, and sulfur trioxide:



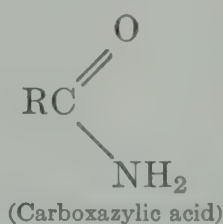
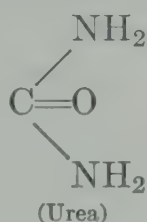
The resulting solutions are acidic, first, because an ammonium salt is formed and second, because a solvo acid is also obtained. So-called solvo acids are of particular interest because many of these substances are incapable of behaving as acids in aqueous solution.

Such solvo acids may be completely ammonated, or only partially ammonated. A substance which is completely ammonated is the nitrogen analog of the corresponding oxy acid and may be called an ammono acid. A substance which is incompletely ammonated and which still retains hydroxyl or oxygen groups in its composition is specifically designated as a mixed aquo ammono acid:

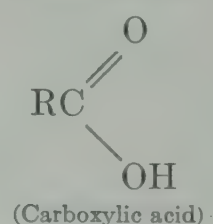
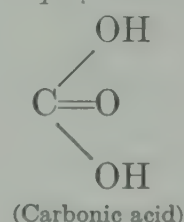
Ammono Acid



Aquo Ammono Acid



Aquo Acid



Franklin (1) has gone even a step further in giving special names to the ammono and mixed aquo ammono acid analogs of the carboxylic acids. The acid amides, RCONH_2 , which are mixed aquo ammono carboxylic acids, are called carboxazylic acids; the amidines, $\text{RC}(\text{NH})(\text{NH}_2)$, being the completely ammonated analogs of the carboxylic acids, are called the carbazylic acids. This nomenclature has not, however, won popular acceptance.

The material which follows is designed to familiarize the reader with the "nitrogen system of compounds." Application of this concept should make it possible to predict the probable behavior of a nitrogen compound when dissolved in liquid ammonia. It should suggest synthetic procedures for preparation of nitrogen compounds or conver-

sion of oxygen compounds into their nitrogen analogs. Chemical relationships among nitrogen compounds as derivatives of ammonia become more obvious. Systematic correlation of nitrogen compounds among themselves and in comparison with their oxygen analogs helps to define the field of nitrogen chemistry more clearly.

AMMONO AND AQUO AMMONO CARBONIC ACIDS (2, 3)

Spectacular success in elucidating the relationships between the various nitrogen derivatives of carbonic acid has been achieved by considering these substances as solvo acids. Just as orthocarbonic acid, carbonic acid, and carbon dioxide are related by processes of dehydration, so can the nitrogen derivatives of carbonic acid be related to each other by processes of ammonation and deammonation, as shown in Figures 3 and 4. The reactions from left to right are deammonation reactions; those in the vertical columns show why the polymers of these intermediates may be classified as ammono carbonic acids. These relationships have served as a guide for the synthesis of many of these compounds. What is even more interesting is that all these substances do behave as acids when dissolved in liquid ammonia, even though their chemical character differs profoundly in aqueous solution.

The question may naturally be raised as to how this particular concept may help in the synthesis of ammono compounds. Information available in the literature may be cited to show how the compounds depicted in Figure 4 may be converted one into the other. Carbon dioxide is converted by direct ammonation to the ammonium salt of carbamic acid. Carbamic acid, specifically its metallic salts, can be made to undergo dehydration at higher temperatures to give the corresponding cyanates. Ammonium cyanate is convertible by intramolecular ammonation into urea. Urea is obtainable by one of the older processes from calcium cyanamide by hydrolysis, a reaction representing a solvolytic reaction in which an ammono carbonate is converted into a mixed aquo ammono carbonate. Cyanamide, on the other hand, will react in liquid ammonia solutions, or at higher temperatures in the fused state, with ammonium salts to give guanidine salts. Carbon tetrachloride will react with ammonia under pressure in the presence of copper to give guanidine.* Carbonyl chloride, which is an acid chloride of carbonic acid, will also undergo ammonolysis to form urea. All the reactions which

* After 16 hours at 300°C. only about 4% of the CCl_4 is converted to guanidine in the absence of copper. (Personal communication from Dr. G. Watt.)

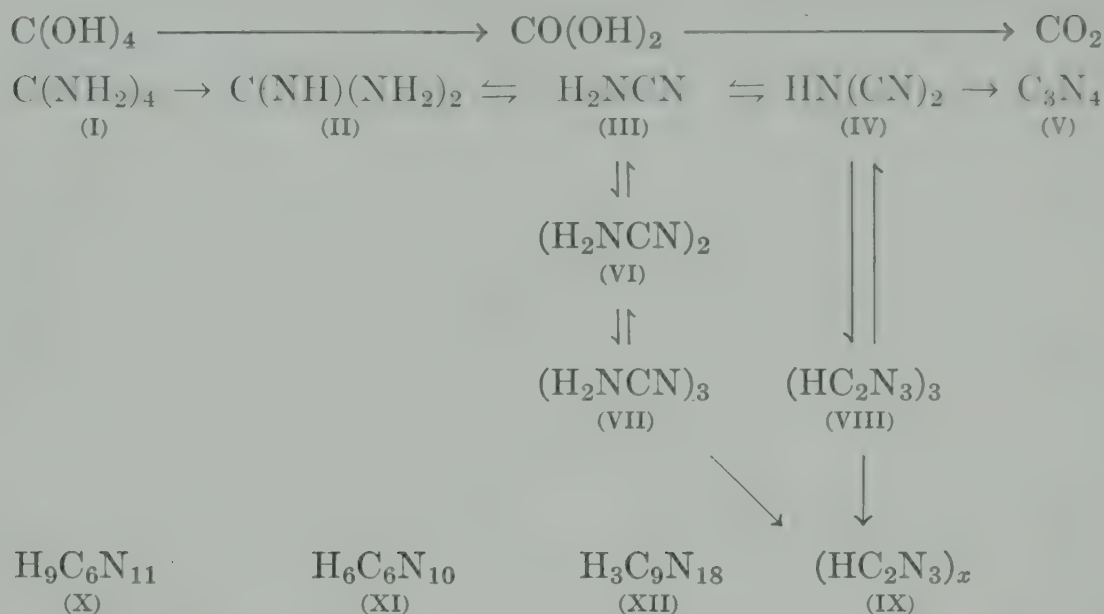


FIGURE 3. The ammono carbonic acids. Relationships in the horizontal rows represent deammonation-ammonation reactions: guanidine(II), cyanamide(III), dicyanamide(IV), carbonic nitride(V). Vertical columns represent polymerization products: dicyandiamide(VI), melamine(VII), tricyanomelamine(VIII), melon(IX). Compounds of indefinite structure, but related to each other as ammono carbonic acids, are melam(X), melem(XI), and hydromelonic acid(XII).

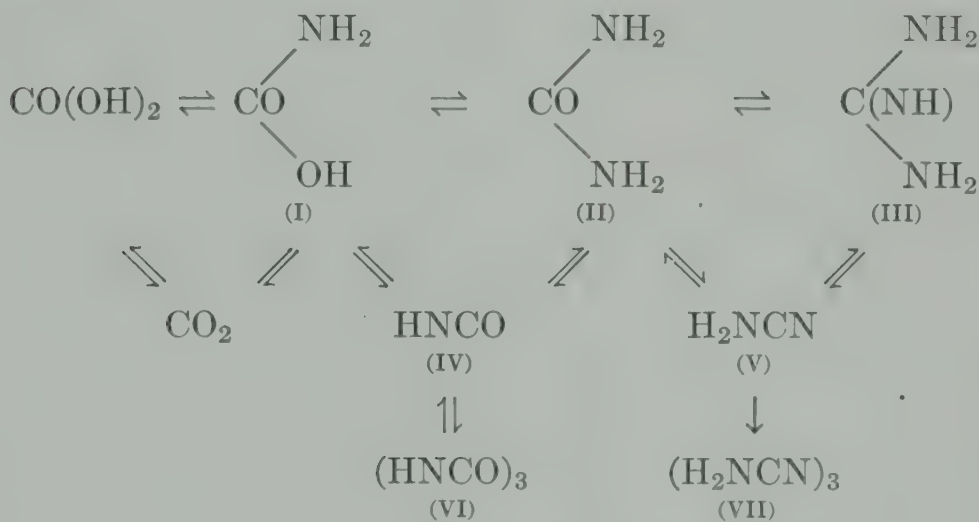


FIGURE 4. The aquo ammono carbonic acids. Ammonolytic products are represented by carbamic acid(I), urea(II) and guanidine(III). Cyanic acid(IV) and cyanamide(V) are desolvation products. Cyanuric acid(VI) and melamine(VII) are polymerization products.

have been cited involve either ammonation, deammonation, or ammonolysis.

NITROGEN ANALOGS OF THE PHOSPHORIC ACIDS (3, 4, 5)

Some of the formal relationships which hold for nitrogen compounds of pentavalent phosphorus are depicted in Figures 5 and 6. Deammonation of the hypothetical compound with the formula $P(NH_2)_5$ leads successively to phosphonitrilamide, phospham, and phosphorus(V) nitride. Phosphorus(V) nitride, an article of commerce,

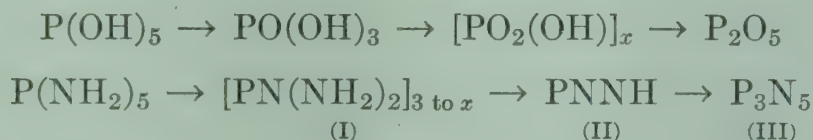


FIGURE 5. The ammono phosphoric acids as deammonation products: phosphonitrilamides(I), phospham(II), and phosphorus(V) nitride(III).

is prepared by the high-temperature reaction of phosphorus(V) sulfide with ammonium chloride in an ammonia atmosphere. Reaction of phosphorus(V) chloride with ammonia undoubtedly leads to the formation of a mixture of phosphonitrilamides which readily undergo desolvation to form an infusible product with the empirical composition HNPN, known as phospham. Not very much is known of these completely ammonated derivatives of pentavalent phosphorus.

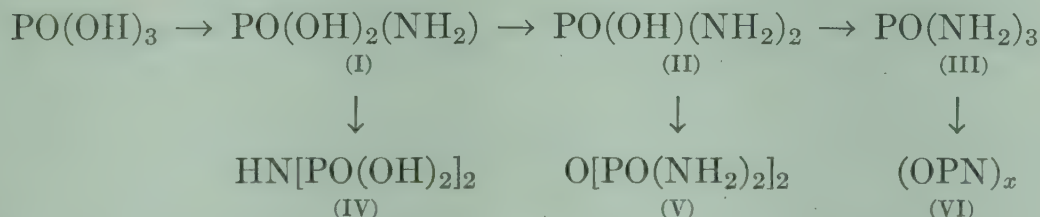


FIGURE 6. Mixed aquo ammono phosphoric acids. Ammonolysis products include amidophosphoric acid(I), diamidophosphoric acid(II), phosphorus(V) oxytriamide(III). Typical desolvation products are given by imidodiphosphoric acid(IV), pyrophosphoryl tetramide(V), and phosphorus(V) oxynitride(VI). Numerous other condensation-polymerization products are possible.

The relationships among the aquo ammono phosphoric acids are more satisfactorily defined. Both amido- and diamidophosphoric acid are unstable crystalline substances. They are synthesized by a rather complicated series of chemical reactions involving ammonolysis of the mono- or dichlorophenylphosphates, followed by treatment with potassium hydroxide to give the corresponding potassium salts, from which the free acids are obtainable. Diamidophosphoric acid is

better characterized than the monoamido derivative. Both undergo rapid hydrolysis and are converted eventually into ammonium phosphates. Although the parent inorganic substances are not very well defined, it is interesting to point out that derivatives of mono- and diamidophosphoric acids in which substituents are organic radicals, both on the oxygen and on the nitrogen atoms, are quite stable and well known (6). The mixed aquo ammono esters are excellent hydrogen bonding agents and, like the esters of phosphoric acid, are capable of serving as plasticizers for cellulose esters and vinyl type polymers.

The N-substituted phosphorus(V) oxytriamides have also long been known. The parent substance, phosphorus(V) oxytriamide, is unknown, even though references in the literature claim that its preparation has been effected. If phosphorus(V) oxychloride is subjected to ammonolysis, a mixture consisting of products related to $\text{PO}(\text{NH}_2)_3$ is obtained. It is doubtful if the intermediate deammonation product, phosphoryl imide amide, $\text{PO}(\text{NH})(\text{NH}_2)$, is actually a definite chemical entity. The end product, phosphorus(V) oxynitride is, however, fairly well established, and should be represented by the formula $(\text{OPN})_x$ to indicate that it is highly polymerized.

One of the most interesting substances in the whole realm of inorganic chemistry is the so-called inorganic rubber. This substance can be prepared by the interaction of phosphorus(V) chloride with ammonium chloride. Only partial ammonolysis occurs with the formation of products, which may be



represented empirically by the formula PNCl_2 . The reaction mixture consists of crystalline and oily polymers. The crystalline polymers can be separated quite readily; the oily material remains to be investigated more carefully. The crystalline material is a mixture of two compounds whose molecular weights and composition lead to the conclusion that they represent a trimer and tetramer, respectively.

From the Franklin point of view, PNCl_2 represents an acid chloride of an ammono phosphoric acid. The chlorine atoms are quite reactive and will undergo characteristic solvolytic reactions with water, with ammonia, with amines, and with alcohols, leading to the phosphonitrilic acids, the phosphonitrilamides, the N-substituted phosphonitrilamides, and the esters of the phosphonitrilic acids. Many examples of such reactions have been disclosed in the literature. Both partial and complete solvolysis may occur, with the result that a variety of solvolytic products is obtainable. All these type reactions

characterize the crystalline trimer and tetramer as well as the more highly polymerized oily materials which presumably represent linear structures. The preparation and properties of the phosphonitrilic chlorides and their derivatives have been reviewed in detail by several authors (7, 8).

What is most interesting about PNCl_2 products, however, is the fact that they undergo polymerization when heated to higher temperatures. The oily products polymerize quite readily, whereas the crystalline materials are less susceptible to polymerization and must be heated to a higher temperature for longer periods of time.

AQUO AMMONO SULFURIC ACIDS (9, 10)

The relationships which characterize the nitrogen analogs of sulfuric acid are depicted in Figure 7. The completely ammonated derivatives

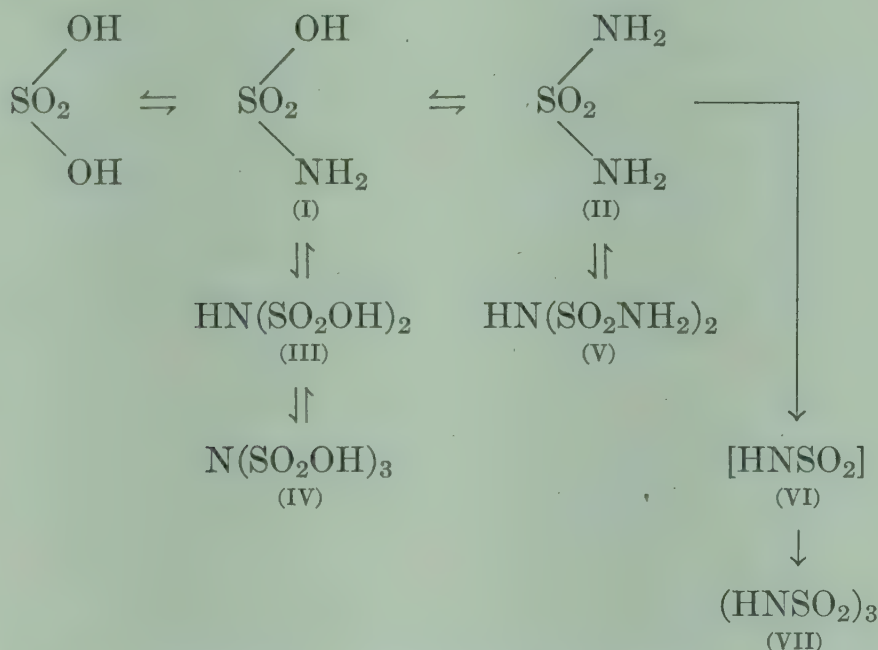


FIGURE 7. The aquo ammono sulfuric acids: sulfamic acid(I) and sulfamide(II) as solvolytic products; imidodisulfuric acid(III), nitridotrisulfuric acid(IV), imidodisulfamide(V), sulfimide(VI) and trisulfimide(VII) as deammonation products.

of hexavalent sulfur corresponding to those of carbon are not known. Replacement of one or both of the hydroxyl groups in sulfuric acid by one or two amide groups, their ammono equivalents, leads respectively to sulfamic acid and to sulfamide. Sulfamic acid is related in turn by deammonation to imidodisulfuric acid and to nitridotrisulfuric acid. Deammonation of sulfamide leads either to imidodisulfamide or, by way of an unknown monomeric sulfimide, to trisulfimide.

It is interesting to point out in this connection that sulfimide like cyanic acid exhibits a marked tendency to undergo stabilization by cyclization. Sulfur in the hexavalent state, like carbon, tends primarily to assume a tetrahedral configuration.

The question may again be raised, Does such a classification or scheme have any basis in actual fact? The answer is definitely in the affirmative; many of the synthetic procedures leading to the nitrogen derivatives of sulfuric acid actually involve reactions of solvation, solvolysis, or desolvation. Sulfur trioxide reacts with liquid ammonia to give largely the triammonium salt of imidodisulfuric acid. At higher temperatures it is claimed that sulfur trioxide and ammonia will combine to form sulfamide, a reaction which is not very different in some of its aspects from the conversion of carbon dioxide into urea by the action of ammonia. Sulfamic acid, which happens to be a relatively new industrial chemical, can also be made by the sulfonation of ammonia derivatives such as urea. Perhaps more interesting in this connection is the fact that it may also be made by ammonolysis of substances such as chlorosulfonate ion and by displacement of donor molecules from compounds which may be given the formula $M \cdot SO_3$. Pyridine-sulfur trioxide, dioxane-sulfur trioxide, and dimethylaniline-sulfur trioxide react with liquid ammonia to give mixtures of ammonium sulfamate and of the triammonium salt of imidodisulfuric acid. Sulfamide, on the other hand, is obtainable by a typical ammonolytic reaction in limited yields by direct interaction of ammonia and sulfuryl chloride. It is probable that the reaction product resulting from sulfuryl chloride and ammonia is largely a mixture consisting of compounds to which the empirical formula $H_2N(SO_2NH)_xH$ may be assigned.

AMMONO BASES (11)

The base types in liquid ammonia are somewhat more obvious, and a bit simpler. Only a few of the metallic amides are readily and easily soluble in liquid ammonia. Strange as it may seem, sodium amide is practically insoluble in ammonia, whereas potassium amide is fairly soluble. Nevertheless, the metallic amides, imides, and nitrides do represent the nitrogen analogs of the corresponding hydroxides and oxides. Some metallic amides precipitate from solution containing an excess of ammonia, which is an integral part of the structure. In other cases products are obtained which are best regarded as ammonous nitrides, resembling the better-known hydrous oxides.

ORGANIC AMMONO COMPOUNDS (12, 13, 14, 15)

It is in the field of organic chemistry that the nitrogen system concept can be applied with greatest utility. Franklin was especially successful in the extension of these analogies to a wide variety of organic compounds. Some of these relationships are depicted in a

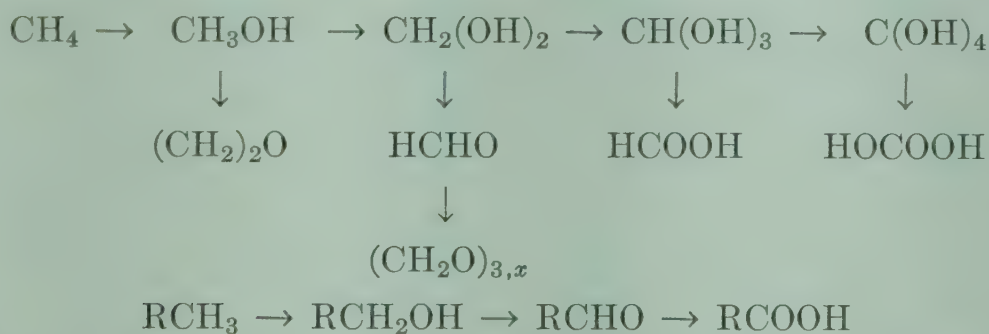


FIGURE 8. Oxygen-containing organic compounds as oxidation (hydroxylation), dehydration, and polymerization products.

somewhat formal way in Figures 8 and 9. In Figure 8 the various classes of oxygen-containing organic compounds are related to the parent hydrocarbon as hydroxylation or oxidation products. This same scheme can be employed to classify organic nitrogen compounds. The hydrogen atoms of methane may be replaced successively by one,

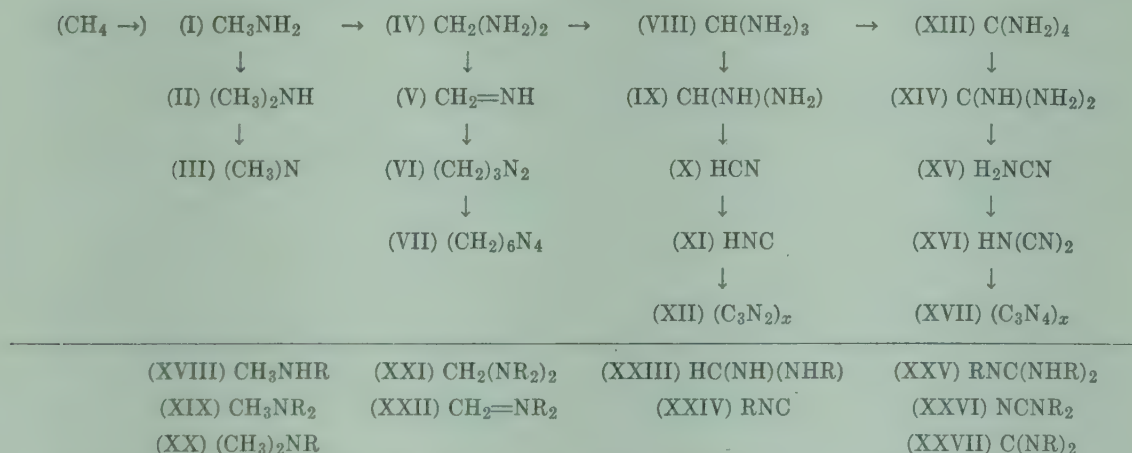


FIGURE 9. Classification of organic nitrogen compounds as ammonio derivatives according to Fernelius and Johnson (13).

two, three, and eventually four NH_2 groups to give the formal analogs of the hydroxylation products. Reactions of ammonation are therefore analogous to those of hydroxylation; nitridation is in the same way related to oxidation. The conversion of methane into guanidine involves a nitridation reaction, just as its conversion into carbonic

acid involves oxidation. The hypothetical ammonation products are in most instances not capable of existence by themselves. The more stable deammonation products are given in Figure 9 and should be compared with the corresponding oxygen compounds in Figure 8.

Fernelius and Johnson (13, 14, 15) have given this subject special consideration in a series of articles dealing with the nitrogen system of compounds, and have summarized these relationships as follows:

"At times, a strict parallelism between nitrogen and oxygen compounds is a bit complicated because of the trivalence of nitrogen as compared with the divalence of oxygen. Also because of this difference in valence, certain derivatives of ammonia have no analogs in the water system, but of the several compounds above [Figure 9], numerous similarities are seen at a glance. Thus (I) and (II) are ammono methyl alcohols, (III) an ammono methyl ether, (IV) the ammonia analog of methylene glycol, (V) an aldehyde-alcohol, (VI) in so far as the two $\text{CH}_2=\text{N}-$ groups are concerned, a formaldehyde, (VII) hexamethylenetetramine, a dimer of ammono formaldehyde, (VIII) ortho ammono formic acid, (IX) the ammonia analog of formic acid, formamidine, (X) formic anammonide, (XI) ammono carbonous acid, (XII) carbonous anammonide, (XIII) ortho ammono carbonic acid, (XIV, XV, XVI) ammono carbonic acids and (XVII) carbonic anammonide. Of those compounds formed by the replacement of a hydrogen atom by a hydrocarbon radical (or by the loss of ammonia between any of these substances and an ammono alcohol), the following are clearly what their names indicate: (XIX, XX) ammono ethers (mixed ethers), (XXI) ammono acetals, (XXII) aldehyde-acetals and esters of (XXIII) ammono formic, (XXIV) ammono carbonous, and (XXV, XXVI, XXVII) ammono carbonic acids."

It is of course dangerous to carry analogies too far. It should be emphasized, however, that the nitridation* or ammonation reactions which serve as the basis for the proposals set forth in Figure 9 are capable of experimental verification in liquid ammonia as a solvent.

The strict consideration of the nitrogen analogs of various organic compounds often leads to unusual conclusions. Suffice it to say that tertiary amines are the nitrogen analogs of the ethers whereas pri-

* It may seem superfluous to use the term nitridation, but nitridation is specifically concerned with a valence change reaction in which a nitrogen-containing radical takes an active part. Many organic reactions involving use of hydrogen azide, substituted haloamides, and hydroxylamine, are nitridation reactions. Each of these reagents is an imide radical donor; the imide radical is the nitrogen analog of active oxygen.

mary and secondary amines are alcohol analogs. Many of the amines, like their alcohol analogs, are capable of entering into coordination with metallic ions. The greater the degree of substitution, the poorer a solvent is the resulting amine for inorganic compounds, and the less highly associated is such a product. Ammono aldehydes exhibit little or no tendency to exist by themselves and will, with facility, undergo deammonation and polymerization. The hypothetical methylene imine, nitrogen analog of formaldehyde, undergoes rapid polymerization to hexamethylenetetramine. Hydrocyanic acid may be regarded as an ammono aldehyde since it will undergo polymerization, and will form addition compounds with bisulfites. It is also an ammono carbonous acid and will undergo nitridation to cyanamide, an ammono carbonic acid, or oxidation to cyanic acid, a mixed aquo ammono carbonic acid, or reaction with sulfur to yield thiocyanic acid, a mixed ammono thiocarbonic acid. Hydrogen cyanide is also the anammonide of formamidine and of formamide.

Reference has already been made to the ammono carboxylic acids. It is obvious that amidines, despite their basic nature in aqueous solution, will behave as acids in liquid ammonia. The acid amides, $RCONH_2$, the thioamides, $RCSNH_2$, will also possess acidic character in ammonia as a solvent. Amidines, acid amides, and thioamides can be made to undergo desolvation to give nitriles, which from the Franklin point of view are the analogs of the organic acid anhydrides.

But there are many other substances of an organic nature which also act as acids in liquid ammonia. Compounds containing the NH_2 group such as aniline, where the attached C_6H_5 radical is negative in character, will dissociate the proton to the solvent ammonia. Diphenylamine is an even stronger acid. Acid character is also manifested more strongly by solutions of amino acids in liquid ammonia.

HYDRONITROGENS AS AMMONO COMPOUNDS (16)

Ammonia is not only the parent substance of a system of compounds, but is also the simplest hydride of nitrogen. As a hydronitrogen it is the nitrogen analog of methane. Some eleven different hydronitrogens are known, of which three, ammonia, hydrazine, and hydrogen azide, have been isolated in the free state. The others are known only in the form of their organic derivatives. The hydronitrogens may be divided into four distinct series based on empirical formulas and on structural considerations. Classification of such chain nitrogen compounds depends upon whether they contain single nitro-

gen-to-nitrogen linkages only, or one, two, and three doubly bonded pairs of nitrogen atoms.

Members of the saturated series of hydronitrogens represented by the type formula N_nH_{n+2} are presented in Table 11. Conventional

TABLE 11

SATURATED HYDRONITROGENS

Type formula: N_nH_{n+2}

NH_3	ammonia	NH_3
N_2H_4	hydrazine (diamide)	H_2N-NH_2
N_3H_5	triazane (prozane)	$H_2N-N-NH_2$
		H
		H
N_4H_6	tetrazane (buzane, hydro-tetrazone)	$H_2N-N-N-NH_2$
		H

structural formulas, together with preferred names and alternative or older names, are also listed. Unsaturated hydronitrogens are listed in Table 12. Relationships within each of the individual series of

TABLE 12

UNSATURATED HYDRONITROGENS

(A) Type formula: N_nH_n

N_2H_2	diimide	$HN=NH$
N_3H_3	triazene (diazamine)	$HN=N-NH_2$
N_4H_4	tetrazene (tetrazone), 2-tetrazene	$H_2N-N=N-NH_2$
N_4H_4	isotetrazene (diazohydrazine, buzylene), 1-tetrazene	$HN=N-NH-NH_2$

(B) Type formula: N_nH_{n-2}

N_3H	hydrogen azide, hydrazoic acid	$HN=N\equiv N$
	azoimide, hydronitric acid, tri-azoic acid	
$N_4H_2?$	diiminohydrazine	$HN=N-N=NH$
N_5H_3	bisdiazamine	$HN=N-N-N=NH$
		H

(C) Type formula: N_nH_{n-4}

N_8H_4	octazotriene (octazone)	$HN=N-N-N=N-N-N=NH$
		H

hydronitrogens are not very definitely marked. There are some similarities between ammonia and hydrazine. There are likewise similarities between the azo and diazoamino compounds, derivatives of diimide and triazene, respectively. A more distinct relationship between various hydronitrogens becomes apparent if the properties of compounds containing the same number of nitrogen atoms are considered. Such parallel relationships recall the similarities between hydrocarbons containing the same number of carbon atoms, as, for instance, between ethane, ethylene, and acetylene. Hydrazine and diimide are related by an oxidation-reduction mechanism. Hydrazo compounds can be oxidized readily to the azo compounds; these, in turn, can be reduced to the hydrazo derivatives. Hydrogen azide, triazene, and triazane are also related in a similar fashion. Organic azides can be reduced to the mono-substituted triazenes, whereas triazanes in turn have been prepared by reduction of certain triazenes.

A still more revealing insight into the nature and properties of the hydronitrogens can be gained from their consideration as the nitrogen analogs of certain of the better-known oxygen compounds. Some of these formal relationships are given in Table 13. Intermediate aquo

TABLE 13

THE HYDRONITROGENS AS AMMONO COMPOUNDS

<i>Ammono Compound</i>	<i>Mixed Aquo Ammono Derivative</i>	<i>Aquo Compound</i>
HNH_2 , ammonia	HOH , water
$\text{H}_2\text{N} \cdot \text{NH}_2$, hydrazine	H_2NOH , hydroxylamine	HOOH , hydrogen peroxide
$\text{HN} \cdot \text{N}_2$, hydrogen azide	$\text{H}_2\text{N} \cdot \text{NO}_2$, nitramide	HONO_2 , nitric acid
$\text{H}_2\text{N} \cdot \text{N} : \text{NH}$, triazene	$\text{HON} : \text{NH}$, hydroxydiimide	HONO , nitrous acid
$\text{H}_2\text{N} \cdot \text{NH} \cdot \text{NH} \cdot \text{NH}_2$, tetra- zane	$\text{HONH} \cdot \text{NHOH}$, dihydroxy- hydrazine; HN(O)NH , oxydiimide	$\text{HO} \cdot \text{O}_2 \cdot \text{OH}$

ammono compounds are also listed. The relationship between hydrazine and hydroxylamine, as the ammono and mixed aquo ammono analogs, respectively, of hydrogen peroxide has certainly been recognized. There is a distinct gradation in chemical properties in going from hydrogen peroxide to hydrazine. Hydrogen peroxide is a more acidic material than either of the nitrogen analogs. Hydrazine, on the other hand, is distinctly an electron pair donor. Hydrogen peroxide serves primarily as an oxidizing agent, whereas hydrazine is distinctly a reducing agent.

Hydrazoic acid is very definitely the nitrogen analog of nitric acid. It is an ammono nitric acid. Ammonolysis of nitrates both in the fused state and also in liquid ammonia solution results in their conversion into azides. Like nitric acid, hydrazoic acid is a powerful oxidizing agent; mixtures of hydrochloric and hydrazoic acid will dissolve the noble metals. Reduction of hydrazoic acid gives a series of products which are strictly analogous to the corresponding reduction products of nitric acid. The mono-substituted azides can be reduced readily to the mono-substituted triazenes. Triazenes, in turn,

A. Reduction of nitric acid:

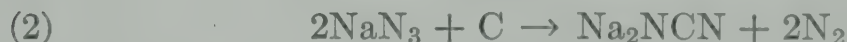


B. Reduction of hydrazoic acid:



suffer reduction by addition reactions to yield the triazanes. Chemical reduction of hydrazoic acid yields in most cases nitrogen and ammonia, less frequently, hydrazine and ammonia. Triazene and hydrazine, as reduction products of the ammono nitric acid, hydrazoic acid, represent the nitrogen analogs of nitrous acid and hydroxylamine, respectively. The intermediate stage between nitrous acid and hydroxylamine, assumed to go through dihydroxyammonia and by desolvation to the nitroxyl radical and hyponitrous acid, is no better defined than the intermediate stage between triazene and hydrazine where a similar desolvation mechanism may lead to a whole series of nitrogen-containing radicals which could conceivably undergo condensation to give any one of a number of hypothetical hydronitrogens.

Hydrazoic acid and its derivatives are excellent nitridizing agents. Fused sodium azide, for instance, will nitridize carbon to yield either sodium cyanide or sodium cyanamide. These reactions involve conversion of carbon into an ammono carbonite and an ammono car-

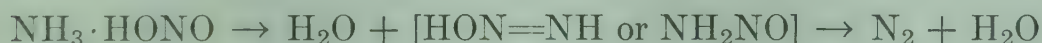


bonate, respectively. In the field of organic chemistry hydrazoic acid and its salts have found widespread use in reactions involving essentially addition of the NH radical. Although the mechanism by which such reactions take place is still open to question, the over-all result

is one which might be expected of hydrazoic acid as a donor of the NH molecule or radical.*

There is another interesting point which is revealed by consideration of hydrazoic acid as an ammono nitric acid. The mixed aquo ammono nitric acid is nitramide, the parent substance of the class of materials known as the nitramines. Organic nitrates, the organic nitramines, and the azides have all found application in the field of explosives. Organic nitrates include materials such as glycerol trinitrate, PETN and DEGN. Lead azide has long been used in fulminating and priming compositions. The newest class of high explosives includes the organic derivatives of nitramide, the best-known example of which is RDX.

Some of the other hydronitrogens may likewise be considered nitrogen analogs of better-known aquo compounds. Triazene is the parent hydronitrogen from which the well-known organic diazoamino compounds are derived. Actually, triazene may be looked upon as an ammono nitrous acid. The intermediate aquo ammono compound, which, for want of a better name, may be called hydroxydiimide, is the parent substance of the diazo compounds and the diazonium salts. Each of these classes of substances is obtained by the action of nitrous acid upon an amine. Such diazotization reactions are therefore solvolytic reactions in which nitrous acid is converted either into a derivative of a mixed aquo ammono nitrous acid or into the triazene, the ammono nitrous acid. Diazonium salts are converted by the action of excess amine into the diazoamino compounds. The thermal composition of ammonium nitrite involves an intramolecular diazotization reaction, with the intermediate formation of hydroxydiimide. The latter is unstable and undergoes the characteristic reaction of compounds of this type, with the liberation of nitrogen and formation of water:



These analogies can be extended to the hypothetical aquo analogs of some of the higher hydronitrogens, even though to do so is somewhat

* Hydrazoic acid may also be regarded as a nitrogen analog of nitrous oxide. Even as nitrous oxide represents a source of active oxygen, so may hydrogen azide be considered to decompose to yield molecular



nitrogen and the active oxygen analog, imide. It is interesting to note in this connection that sodium azide is prepared by an ammonolytic reaction involving interaction of nitrous oxide and sodium amide: $2\text{NaNH}_2 + \text{N}_2\text{O} \rightarrow \text{NaN}_3 + \text{NaOH} + \text{NH}_3$.

speculative. Tetrazane may also be related to a hypothetical dihydroxyhydrazine, which, by a process of dehydration, would lead to a hydronitrogen which is the parent substance of the azoxy compounds. Tetrazane could also be regarded as the nitrogen analog of a hypothetical hydride of oxygen with the formula H_2O_4 . Certain of the alkali polyoxides were at one time given formulas corresponding to such an unknown ozonic acid. It has now been rather definitely established that these have the simpler molecular formula, MO_2 . Oxygen exhibits even a lesser tendency to undergo self-linkage than nitrogen. If an H_2O_4 structure were to be postulated for such a polyoxide, one would expect it to dissociate and possibly exist only as a free radical-type substance. On the basis of magnetic measurements a free radical-type structure is now assigned to the metallic superoxides. The fact that the tetrazanes exhibit some tendency to dissociate to give hydrazyl radicals in solution does lend some credence to what might otherwise be regarded as mere speculation.

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REACTIONS IN LIQUID AMMONIA

Experimental Techniques and Some Important Type Reactions

No other solvent, with the exception of water, has been subjected to more thorough experimental study with respect to its potentialities as a reaction medium than has liquid ammonia. All manner of metathetical reactions can be carried out in liquid ammonia. Some of these depend on the fact that solubility relationships in liquid ammonia differ from those which characterize water and thus permit the formation of some particular compound not precipitated in an analogous reaction in water. In other instances compounds which are incapable of existence in other solvent media can be prepared. This is especially so among the ammono and mixed aquo ammono compounds whose true character as acids and bases is revealed by their behavior in liquid ammonia as a solvent. Even more important than such ionic reactions are the reactions of ammonolysis, ammonation, and deammonation, involving solvolytic, solvation, and desolvation reactions, similar in nature to reactions of hydrolysis, hydration, and dehydration. Each of these types of reactions is particularly important in effecting the synthesis of nitrogen compounds. Although reactions of ammonolysis and ammonation can be carried out in the vapor state and in other solvents (even water), the present discussions are limited to those in which liquid ammonia serves as both solvent and reaction medium.

Use of liquid ammonia as a solvent and reaction medium entails no complicated experimental techniques. Because of the low boiling point and the toxicity of liquid ammonia it is necessary to modify conventional procedures, first, in order to carry out reactions at lower temperatures or under pressure and, second, to protect the operator either by working under a hood or in a closed system. Some special considerations covering techniques applicable to liquid ammonia are, therefore, taken up briefly before reactions of metathesis, ammonoly-

sis, ammoniation, and the behavior of acids and bases are reviewed in more detail.

TECHNIQUES IN LIQUID AMMONIA

Ammonia is a *toxic material*. An ammonia-type gas mask should always be available and near at hand should an accident occur necessitating operation in an ammonia atmosphere.

Despite the fact that ammonia has a low boiling point at atmospheric pressure, it does not evaporate rapidly since its heat of vapori-

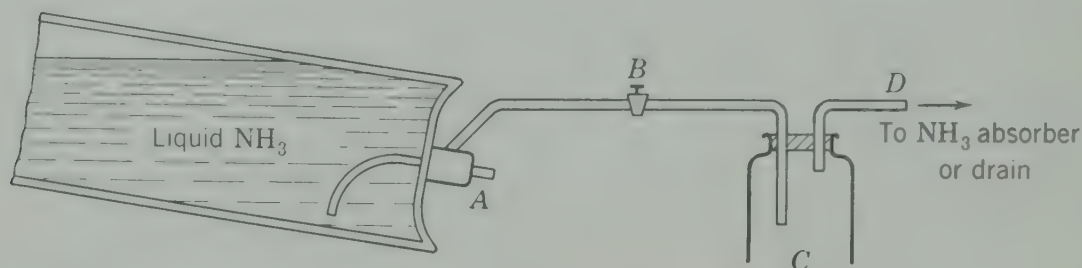


FIGURE 10. Conventional-type ammonia tank depicting main valve *A*, steel needle valve *B* for regulating flow of ammonia, receptacle *C*, and outlet *D* to an ammonia absorber or through a safety trap to the drain (where excess ammonia can be carried off by water).

zation is exceptionally high. Conventional laboratory equipment can be used for many of the operations involving use of the liquid at atmospheric pressure. It is not necessary to use vacuum-jacketed vessels; if these are not used, however, it is desirable to employ cooling baths so that reactions can be moderated. Reagents should also be cooled before being added to liquid ammonia.

Synthetic ammonia should be specified. By-product ammonia contains a not inconsiderable amount of water and other impurities.

Two varieties of ammonia tanks are available for laboratory use. The most common type is depicted in Figure 10. The ammonia can be withdrawn directly as a liquid by placing the tank upon a standard so that the outlet tube is in the position indicated in the diagram. In order to control more readily the flow of liquid from the tank it is desirable to place a steel needle valve in the outlet system. It often happens that rapid evaporation of the liquid ammonia under pressure to effect reduction in temperature to the normal boiling point upon release from the tank causes the main valve stem to cool quite markedly, with the result that moisture condenses on it and even freezes. It then becomes exceedingly difficult to turn the main valve; the subsidiary steel valve in the line constitutes a safeguard against such a

possible danger. In withdrawing the ammonia from the tank the main valve on the tank itself is first opened, while the subsidiary valve is kept closed. The subsidiary valve is then opened and the flow adjusted thereby so that the liquid runs directly into a Dewar flask. It is usually desirable to use an unsilvered one-liter Dewar flask fitted snugly with a two-holed stopper. The tank outlet is passed through one hole of the stopper with which the Dewar flask is fitted. A connection is made through the other hole to a safety trap and thence either to a water pump or into the drain through which water is being run to carry off the ammonia gas. Under no circumstances should any of the metal parts, valves, fittings, or tubing be made of copper or copper alloys. These are rapidly corroded by ammonia.

The "X"-type cylinder operates like a carbon dioxide tank. It can be placed in an upright position next to the desk; by opening the valve appropriately liquid ammonia can be obtained directly. The tank operates as a siphon tube device; when the valve is opened liquid ammonia is forced up through the inner steel tube. This tank occupies less space in the laboratory and is more convenient to use.

Ammonia can be dried, prior to condensation, by passing the gas over such desiccants as barium oxide, soda-lime, or sodium wire. It is simpler, however, to dissolve metallic sodium directly in liquid ammonia and then distil the dry ammonia therefrom. Metallic sodium will react completely with any water which is present; the resulting ammonia gas is completely anhydrous.

In order to carry out reactions at ordinary pressures it is necessary to operate at the normal boiling point of liquid ammonia, $-33^{\circ}\text{C}.$, or below. Flasks, beakers, and ordinary laboratory apparatus can be used in those instances where moisture has no effect upon the reaction product and where it is merely desirable to use ammonia because of its solvent properties. Even those reactions involving use of sodium in liquid ammonia can be run in ordinary equipment since a slight excess of sodium will facilitate removal of dissolved moisture. Büchner funnels can be used for filtration, provided that the funnel and the receptacle are cooled thoroughly before actual use. It is also necessary to use a rather powerful water pump to draw off the ammonia rapidly to effect filtration. In some instances the procedure of inverted filtration is more convenient. The general availability of such inverted filters of fritted glass makes this procedure desirable where some protection from the atmosphere is required. As a substitute a paper extraction thimble (such as is used in Soxhlet extractors) can be placed in position to surround the end of a glass tube and employed to effect what amounts to inverted filtration.

Among the very unusual reactions which can be carried out in liquid ammonia are those involving the extent of reduction of substances by alkali metal solutions and the determination of the amount of gas which may be evolved as a result of such reactions. The apparatus described by Fernelius and Johnson (1) and more recently modified and refined by Watt and his students (2, 3) is admirably suited for general use in the laboratory. The simpler set-up is depicted in Figure 11. For carrying out many reactions in ammonia at its normal boiling temperature, a reaction tube of the type shown in Figure 11 is quite satisfactory. According to Fernelius and Johnson (reference 1, p. 444):

"In order to maintain the temperature of the vessel at the boiling point of ammonia, it is placed in a Dewar tube to the level *H* and attached to the latter by a rubber stopper fitting. A piece of glass tubing fitted through a small hole in the stopper allows the ammonia gas from the Dewar flask bath to escape into a waste line which runs into a container of water.

"In order to condense ammonia at its boiling point, the gas must be supplied at a pressure of several centimeters above that of the atmosphere. This is accomplished by allowing the ammonia to enter the reaction vessel against a column of mercury of about 20 centimeters, since the other side of the mercury column is open to the atmosphere. Such a scheme is shown in Figure 11. The mercury column at *I* may be increased or decreased by raising or lowering a leveling tube *K* containing mercury which is connected to *I* by means of pressure tubing."

Johnson and Fernelius illustrate by means of a specific example how this apparatus can be used to study the course of a reaction. The illustration employed involves the reaction between ammonium bromide and metallic sodium dissolved in liquid ammonia. The reaction which takes place can be represented by the following equation:



They write (reference 1, p. 445):

"Ammonia gas is first allowed to pass through the tube at stopcock *A* to the bottom of the reaction vessel through tube *F* until all the air has been displaced in the system. With a small stream of gas still flowing and the cap on the side tube removed at *C* (ground glass joint), a freshly cut piece of sodium is introduced through the opening and falls to the bottom of the reaction vessel *E*. The side tube is put back into position and fastened securely by means of rubber bands which

are strung between the corresponding ears shown in the figure. The mercury bulb *K* is then raised, with stopcock *J* open, to increase the height of the column. The reaction tube is then set into a Dewar tube in the manner previously described. The pressure of the ammonia gas coming from the storage cylinder is increased sufficiently by this procedure to condense the vapor in *E*. The tube *F* soon be-

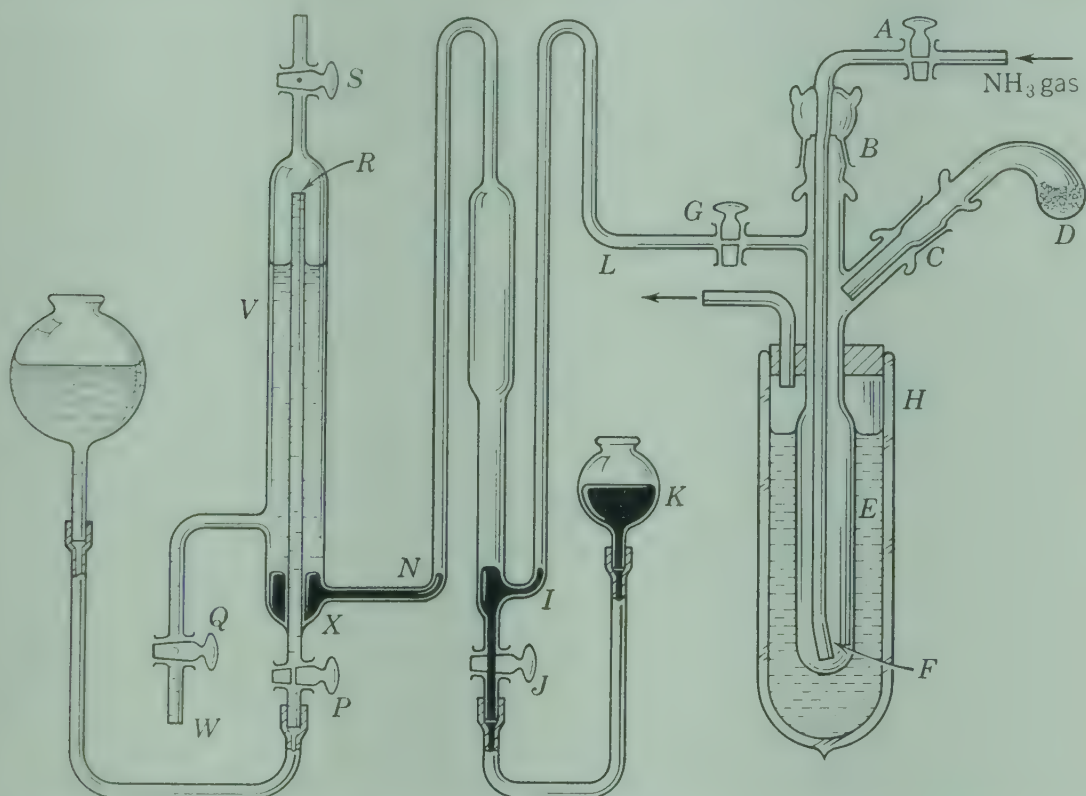


FIGURE 11. Apparatus for carrying out reactions in liquid ammonia according to Fernelius and Johnson.

comes surrounded with liquid, and the ammonia gas bubbles through at the extreme end to keep the liquid ammonia solution of sodium well agitated. When several cubic centimeters of the liquid are present in *E*, the mercury column *I* is again lowered to prevent further condensation of the ammonia vapor and the pressure of the gas at the tank is decreased so that only a slow stream stirs the solution at *F*. The side tube containing dry ammonium bromide at *D*, having been previously weighed, is now turned about the ground glass connection *C* as an axis through an angle of about 120° so that by gentle tapping small pieces of the ammonium bromide are introduced into the solution below. The solution is well stirred, and ammonium bromide is added slowly until the blue color of the dissolved sodium has been discharged completely.

"The dissolved sodium serves as a good indicator for the reaction since only a small part of a milligram in solution is sufficient to produce a blue color. As soon as the color has disappeared, the tube may be reweighed and the amount of ammonium bromide used determined by difference. From this value may be calculated the amount of sodium that took part in the reaction.

"According to the above equation, every mole of ammonium bromide liberates one-half mole of hydrogen gas. Figure 11 shows how this gas may be collected and the volume determined. The tube *V* is filled with air-free water and contains a small amount of mercury at the bottom which serves as a trap. The tubes *P* and *W* connect to bulbs containing water open to the atmosphere. At *X* the small tube *R* is sealed inside the larger tube *V*. This construction gives a means for introducing water during the course of the reaction through *P* and thus through *R* and at the same time for withdrawing ammonia solution at *W*. In this way the water that is saturated with ammonia may be replaced by fresh water.

"The hydrogen gas liberated in the reaction tube is carried out of the tube by a fairly rapid stream of ammonia gas through *L*, through the mercury at *I*, and over to the collecting tube *V*. The hydrogen displaces the water and the ammonia is absorbed. If tube *V* is calibrated, an estimate of the amount of hydrogen liberated may be made providing the partial pressure of the water and ammonia vapors are taken into consideration. An accurate determination may be made by opening stopcock *S* and allowing the mixture of gases to pass over phosphorus pentoxide to remove both water and ammonia."

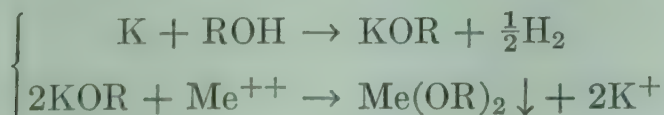
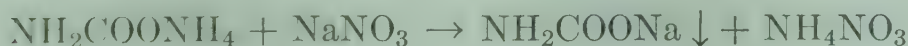
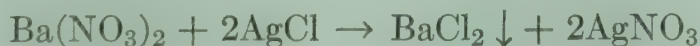
Many reactions must be carried out under pressure. Closed-tube reactions can often be used in the laboratory. Certain precautions should be observed in sealing off tubes containing any liquefied gas (4). Liquid ammonia, it should be noted, has a relatively high coefficient of expansion; no tube should be filled more than two-thirds full. To facilitate the sealing operation that portion of the tube which contains the liquid ammonia is immersed below the surface of the cooling bath. The seal should be annealed carefully and allowed to cool completely before the tube is removed from the cooling bath. The individual tubes should be encased in wire screen forms so that injury from flying glass can be avoided should the tubes burst. The operator should wear protective goggles and wire-reinforced asbestos gloves, if sealed tubes must be handled. If tubes are to be shaken they must be handled behind a protective screen.

If a closed tube has been allowed to come to room temperature or higher to effect more rapid reaction it is absolutely necessary that the tube be cooled first to below -33°C . before it is opened. A hot wire or a glass rod can then be applied to a file scratch to crack the tube. It is often desirable subsequently to transfer the contents of such a tube to some convenient container. This can be done by inserting the tube through a rubber stopper which fits in turn a conveniently sized filter flask. The whole set-up is rapidly inverted, the ammonia solution transferred to the filter flask, after which the gas is allowed to evaporate from the filter flask into an absorbent.

Equipment of all sorts is now available for carrying out reactions in larger quantities under pressure. Standard high-pressure equipment can be used for liquid ammonia reactions provided no copper gasketing material, liners, or tubing are employed. Reactions involving the use of liquid ammonia should be carried out in glass-lined or steel autoclaves. Lead gaskets have been found to work rather well. For ordinary operations which involve heating only up to room temperature a laboratory autoclave of about one liter capacity may be used (5, 6). Various special textbooks may be consulted for information concerning laboratory techniques involving use of liquefied gases (1, 7, 8, 9, 10).

METATHETICAL REACTIONS

Unusual solubility relationships in liquid ammonia frequently lead to reactions which are completely different from those which occur in aqueous solution (11). Thus, for instance, silver chloride and barium nitrate are both soluble in liquid ammonia; when solutions of the two are brought together, it is barium chloride which precipitates. In like fashion the slightly soluble ammonium carbamate obtained by passing carbon dioxide directly into liquid ammonia (or by adding Dry Ice to the solvent) reacts with sodium nitrate to precipitate sodium carbamate. Direct reaction of metallic potassium with the lower alcohols results in the formation of the corresponding potassium alcohates. These will react with other metallic salts to yield metallic alcohates which cannot be prepared in any other way (12):



One of the earliest attempts (13) to survey the possibilities of metathetical reactions in liquid ammonia involved a qualitative study of the interaction of various ammonium salts [NH_4Cl , NH_4Br , NH_4I , $(\text{NH}_4)_2\text{S}$, $(\text{NH}_4)_2\text{CrO}_4$] with nitrates of the common metallic elements (Li, Na, K, Ca, Sr, Ba, Mg, Mn, Co, Zn, Ni, Cd, Hg, Pb, Ag, and Cu). Observations were recorded giving the colors of the precipitates so obtained. The exact composition of these precipitates was not determined, but, even so, some very interesting synthetic procedures appear to be revealed thereby. Lithium chloride is precipitated from a concentrated solution of lithium nitrate by addition of ammonium chloride. This is also true in the case of manganese and cobalt. An immediate violet precipitate is obtained when ammonium chloride is added to a solution of nickel nitrate. There is less tendency for precipitates to form when ammonium bromide and ammonium iodide are added to these same metallic salts. This is in line with the generalization that iodides are more soluble than the bromides and chlorides.

Perhaps most surprising, however, are the reactions which occur when ammonium sulfide is used as reagent. Hydrogen sulfide is readily soluble in liquid ammonia. Precipitates are obtained immediately when hydrogen sulfide is added to solutions of strontium and barium salts. Precipitates form slowly with calcium and magnesium salts. Addition of hydrogen sulfide to a cobalt salt solution in liquid ammonia gives a pinkish precipitate which turns black on the addition of water. In the case of copper, a yellowish precipitate is obtained. It is probable that ammoniated sulfides * are first formed in each of these cases.

It seems not improbable that some of the unusual precipitation reactions which have been recorded for liquid ammonia may also hold for amine solvents which can be used at room temperatures. Certainly, a more thorough investigation of the exact nature of the materials which are obtained in these precipitation reactions is in order. It might also be worth while under the circumstances to consider the use of the sodium salts of the precipitants rather than the ammonium (or onium) salts which represent acidic substances in ammonia (or amine) as the solvent.

REACTIONS OF ACIDS IN LIQUID AMMONIA

It has already been pointed out that the ammonium ion is the analog of the hydronium ion and that any potential proton donor will

* Reference is made to the fact that the sulfides of arsenic, antimony, and of tin(IV) are soluble in liquid ammonia.

undergo reaction with the solvent ammonia in accordance with the equation



Ammonium salts are therefore acids in liquid ammonia. In view of the fact that ammonia is a basic solvent, acid character of proton donors will be enhanced compared with the behavior of these same compounds in water. Such substances as urea and guanidine behave as acids in liquid ammonia despite the fact that they are bases in water. Ammonia, however, is a solvent of low dielectric constant; the percentage ionization of electrolytes is therefore very much less at comparable concentrations in ammonia than it is in water. Whereas acid character may be developed in a weak proton donor, it is significant that acid strength is lower for all acids in ammonia as the solvent. Ammonia is more an acid-leveling rather than an acid-differentiating solvent.

It should furthermore be pointed out that no abnormal ionic mobility has been observed for the hydrogen ion in liquid ammonia. The conductances of the ammonium ion and of ammonium salts lie in the same range as those of the potassium and sodium ions and the corresponding salts (see Table 14).*

TABLE 14

EQUIVALENT CONDUCTANCE OF SOME INORGANIC ELECTROLYTES

	Δ_0	
	<i>in NH₃ (liq.) at -33°C. in H₂O at 18°C.</i>	
HCl	310	380
NaCl	309	109
HBr	303	381
NaBr	302	110.5
HNO ₃	302	~376
NaNO ₃	301	~105
KNO ₃	339	~126

In addition to the ammonium salts which represent the Brönsted acids in liquid ammonia attention should be called to the amido and imido derivatives of non-metallic elements which constitute the typical solvo acids of the nitrogen system. Methods for the preparation of some of these solvo acids are discussed in more detail under reac-

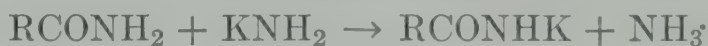
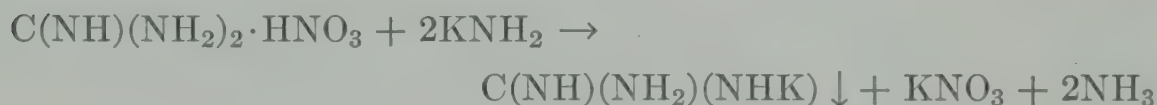
* Mobility of the solvated proton is not abnormal in other amine solvents. The extraordinarily high mobility of the solvated hydrogen ion in aqueous solution is due to an entirely different and unusual mechanism which apparently is exhibited only in water and in some of the more acidic solvents.

tions of ammonolysis and ammonation (page 82). The action of ammonia on a non-metallic halide, sulfide, oxyhalide, thiohalide, and upon halo acids, as well as upon esters and other organic compounds containing reactive groups, leads to the formation of ammono and mixed aquo ammono acids. Typical examples are given in Table 15.

TABLE 15
FORMATION OF AMMONO ACIDS

<i>Reactant</i>	<i>Product</i>
BCl_3	$\text{B}(\text{NH}_2)_3, \text{B}_2(\text{NH})_3$
PCl_5	$[\text{PN}(\text{NH}_2)_2], (\text{HNPN})_x$
SO_2Cl_2	$\text{SO}_2(\text{NH}_2)_2, \text{NH}_2(\text{SO}_2\text{NH})_x\text{H}$
NaSO_3Cl	NaSO_3NH_2
$(\text{RO})_2\text{POCl}$	$(\text{RO})_2\text{PONH}_2$
$\text{RCOX} \quad \left. \begin{array}{l} \text{RCOOR}' \end{array} \right\}$	RCONH_2
$\begin{array}{c} \text{OR} \\ \diagup \\ \text{RC} \\ \parallel \\ \text{NH} \end{array}$	$\text{RC}(\text{NH})(\text{NH}_2)$

Ammonium salts, ammono acids, and mixed aquo ammono acids will react with various metallic amides, imides, oxides, and hydroxides to produce salts (7, 11). The reaction between potassium amide and ammonium chloride to give potassium chloride is a typical neutralization reaction. Potassium amide will also react with ammono and aquo ammono acids, for example, guanidine, acid amides, and sulfamic acid, to give the corresponding potassium salts:



Reference has already been made to the solution of ammonium nitrate in liquid ammonia known as Divers' solution; it is stable at temperatures approaching room temperature. Such a solution of ammonium nitrate in liquid ammonia represents a highly concentrated solution of nitric acid in liquid ammonia. Divers' solution dissolves potassium and sodium hydroxides, and the oxides of calcium, magnesium, zinc, cadmium, copper, and mercury to give nitrates which are soluble in the ammonium nitrate-liquid ammonia mixture. Metals react to effect reduction to nitrite.

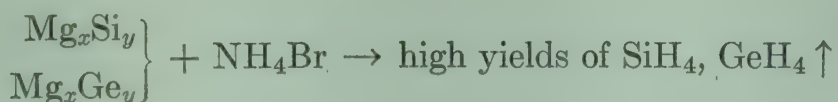
Ammonium salts and ammono acids also react with metals. Solutions of the alkali and alkaline earth metals in liquid ammonia react quantitatively with various ammonium salts, with the evolution of hydrogen:



Since these metal solutions have a characteristic blue color, addition of an ammonium salt can be continued as a titration to the disappearance of the color (see Figure 11). Metallic azides are obtained when ammonium azide in liquid ammonia reacts with lithium, potassium, sodium, calcium, and magnesium. Zinc dissolves slowly in an ammonium azide solution, but aluminum and tin do not react (14).

Solutions of ammonium salts in liquid ammonia bring about the corrosion of various metals (15) and of alloys (16). Manganese dissolves in solutions of ammonium cyanide, bromide, and nitrate. Lanthanum and cerium are dissolved by a solution of ammonium iodide; iron dissolves in an ammonium cyanide solution; cobalt and nickel are soluble in an ammonium nitrate solution; beryllium is attacked by solutions of ammonium chloride, bromide, iodide, cyanide, and thiocyanate.

Ammonium salts have been used for preparative reactions involving the formation of various non-metallic hydrides. Both magnesium silicide (17, 18) and magnesium germanide (19, 20) react with ammonium bromide in liquid ammonia to give high yields of the lower silanes and germanes:



Sodium arsenide reacts with a solution of ammonium bromide in liquid ammonia to produce arsine (21):



REACTIONS OF AMMONO BASES

A number of very interesting reactions involving use of solutions of potassium amide * in liquid ammonia have been carried out by Frank-

* Sodium amide is practically insoluble in liquid ammonia. This does not mean that sodium amide cannot act as a base. The true character of sodium amide as an ammono base is perhaps obvious from a consideration of its reactions at higher temperatures in the fused state.

lin and his co-workers (7). Reactions of potassium amide with such salts as silver nitrate, lead iodide, mercury(II) iodide, bismuth iodide, and thallium(I) nitrate result in the formation of silver amide, lead imide, mercury(II) nitride, bismuth nitride, and thallium(I) nitride, respectively. From solutions of barium salts the corresponding amide, $\text{Ba}(\text{NH}_2)_2$, is precipitated. Aluminum salts react to form a mixed imide-amide. Amides are obtained from some metallic ions, imides from others, and nitrides in a large number of instances. Reactions in liquid ammonia afford the only known means for preparing nitrides* of the more noble metals. It is interesting to note that the metallic amide is usually not obtained where the corresponding hydroxide likewise does not appear to form. For example, Hg_3N_2 and HgO are the reaction products of amide and hydroxide ions, respectively, with the mercury(II) ion.

It might be well to add a word of caution about some of these nitrogen analogs of the oxides and hydroxides. The nitrides of bismuth, mercury, and thallium are very explosive. The exact composition of the so-called fulminating metals, that is, the products obtained when various noble metal compounds are treated in basic solution with aqueous ammonia, is not known, but it is probable that these are compounds containing metal-to-nitrogen linkages.

Many noble metal nitrides decompose at lower temperatures than the corresponding oxides. The nitrides of the highly refractory elements, on the other hand, have even higher melting points than the corresponding oxides.

It is not surprising (now) to find that many of the insoluble metallic amides exhibit amphoteric behavior† in that they dissolve in an

* As nitrides are subjected to more thorough investigation, it may be expected that they will exhibit a whole range of types from ionic to covalent in character, with the probability that the covalent nitrides will be more common, because of the higher formal negative charge on the nitrogen atom. The ionic or covalent character of the nitrides will be determined by the size and formal charge of the associated cation. The greater polarization occasioned by the fact that the nitride ion has a higher charge simply means that ionic nitrides will be fewer in number. This is evident from the fact that many of the nitrides and their more completely ammoniated products, the amides, are amphoteric in character as opposed to the corresponding oxides and hydroxides. Even sodium amide exhibits amphoteric character in liquid ammonia. The interrelationship between the greater degree of polarization of the nitride ion and the more covalent character of amides and nitrides as compared with oxides and hydroxides of the same elements does not appear to have been taken into consideration heretofore.

† Many textbooks still refer to amphoterism as a characteristic reaction of the hydroxyl ion. Amphoterism may be defined in this sense in a very limited way. It is now generally assumed that the solution of an insoluble hydroxide

excess of potassium amide, with the formation of soluble amido complexes. Unusual is the fact that many of these products can be crystallized from solution. The compositions of some of these products are given in Table 16. Even sodium amide appears to dissolve in a potas-

TABLE 16
AMPHOTERIC AMIDES

<i>Franklin Formulation</i>	<i>Resolved Formula</i>
$K_2NNa \cdot 2NH_3$	$2KNH_2 \cdot NaNH_2$
$KNSr \cdot 2NH_3$	$KNH_2 \cdot Sr(NH_2)_2$
$KNBe \cdot 2NH_3$	$KNH_2 \cdot Be(NH_2)_2$
$K_2Zn(NH)_2 \cdot 2NH_3$	$2KNH_2 \cdot Zn(NH_2)_2$
$AgNHK \cdot NH_3$	$KNH_2 \cdot AgNH_2$
$PbNK \cdot NH_3$	$KNH_2 \cdot PbNH$
$Al(NH)(NHK) \cdot 2NH_3$	$KNH_2 \cdot Al(NH_2)_3$
$Ga(NHK)(NK) \cdot 3NH_3$	$2KNH_2 \cdot Ga(NH_2)_3$

sium amide solution. It is interesting to note, in this connection, that the melting-point diagram for the system sodium amide-potassium amide reveals the existence of a stable compound whose composition can be represented by the formula $NaNH_2 \cdot 2KNH_2$. This also appears to be the composition of the product obtained from liquid ammonia.

The insolubility of sodium amide in liquid ammonia has not been a deterrent to its use in this solvent. The reaction between sodium and liquid ammonia is catalyzed tremendously by traces of finely divided metals such as iron, cobalt, and nickel. Under these circumstances sodium amide is precipitated as an insoluble product. The reaction proceeds quite rapidly and thus affords a very convenient method for preparation of sodium amide. Suspensions of sodium amide can be produced in ammonia and the solvent then displaced with some higher-boiling inert liquid in which the desired reaction can then be carried out.*

involves formation of an hydroxo complex and may be looked upon as an example of stabilization through coordination. The formation of a soluble hydroxo complex does not differ in mechanism from the formation of a soluble cyano complex, by reaction of an insoluble cyanide with excess cyanide ion, or the preparation of chloro, bromo, and thio complexes of the elements.

* Bergstrom and Fernelius (22) have published two very comprehensive reviews covering the chemistry of the alkali metal amides. The preparation and properties of the amides are taken up in detail, and this material is supplemented with a survey of inorganic and organic reactions. Many of these reactions involve use of liquid ammonia.

AMMONOLYTIC REACTIONS

Reactions of ammonolysis are of considerable importance as synthetic procedures for the preparation of various nitrogen compounds. Ammonolytic processes are reactions of solvolysis in which ammonia is employed as a reactant to introduce the NH_2 , NH , or N group or ion into a compound by replacement of some reactive element or radical, such as halogen, sulfur, oxygen, or an alkoxy group. Ammonolysis reactions result in a change in the concentrations of ammonium and amide ions in liquid ammonia, just as hydrolysis reactions bring about a change in $p\text{H}$ because of the formation of products which either remove or increase the concentration of one of the characteristic ions of the solvent water.

Ammonolytic reactions depend upon the autoionization of the solvent, which can be represented by the equilibrium:



Self-ionization of ammonia takes place only to a very limited extent as indicated by the fact that the dissociation constant is approximately 10^{-33} . This value is much smaller than for the hydroxylic solvents, and it explains why certain inorganic salts such as aluminum cyanide can be prepared in liquid ammonia as solvent and also why solutions of the alkali and alkaline earth metals in ammonia are capable of existence.

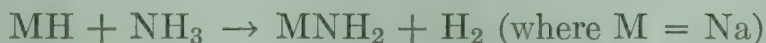
Many reactions of hydrolysis are subject to acid or basic catalysis. Special reference will be made to the fact that analogous reactions of ammonolysis (and aminolysis) may also be catalyzed by the corresponding ammonium and amide ions representing the acid and base analog types of ions in liquid ammonia.

Ammonolytic reactions may be carried out in the vapor state, in the presence of some other solvent such as alcohol, benzene, or water, or in liquid ammonia. Vapor phase "aminations," which are practiced widely in industry, represent a very important type of procedure for the production of nitrogen compounds. Such reactions have been discussed in detail by Groggins (23) and have also been the subject of annual reviews in *Industrial and Engineering Chemistry*. The present discussion, however, will be limited to those ammonolytic reactions which take place in liquid ammonia, either at or below the boiling point at atmospheric pressure, or at higher temperatures under super-atmospheric pressure conditions. These represent liquid phase ammonolytic reactions.

The subject matter dealing with ammonolytic reactions is divided into inorganic and organic reactions, respectively. The presentation which follows is to a large extent based upon the organization of published researches as developed by Fernelius and Bowman (24) in their excellent and comprehensive review entitled, "Ammonolysis in Liquid Ammonia." *

A. AMMONOLYSIS OF INORGANIC COMPOUNDS

HYDRIDES. It is stated that the alkali metal hydrides undergo ammonolysis, with formation of the corresponding amides and hydrogen in accordance with the following equation:



Covalent hydrides, on the other hand, behave as acids in liquid ammonia; the tendency to form the onium salt depends upon the acid strength of the hydride. The halogen hydrides are converted completely into the corresponding ammonium salts. Compounds such as monogermane, monosilane, and phosphine are only slightly soluble in liquid ammonia. Arsine is somewhat more soluble and will react with a solution of metallic sodium in liquid ammonia to give a stable monosodium arsinide. Diborane and tetraborane, on the other hand, are extremely soluble and are converted into crystalline compounds which may be represented as the di- and tetra-ammoniates, respectively.

OXIDES. Sodium monoxide is said to react with ammonia to form sodium amide and sodium hydroxide. Covalent oxides, on the other hand, undergo ammonation. Carbon dioxide reacts with liquid ammonia to give an insoluble precipitate of ammonium carbamate (25). Sulfur trioxide and sulfur trioxide addition compounds with tertiary amines react to give mixtures of ammonium salts of imidodisulfuric acid and sulfamic acid (26). The exact structure of the product obtained from phosphorus(V) oxide has not yet been determined, but a substance having the composition represented by the formula $3P_2O_5 \cdot 8NH_3$ is manufactured and sold commercially under the trade name of Victamide (27).

SULFIDES. Very little work has been done on the reaction of sulfides with liquid ammonia. A number of covalent sulfides, such as those of arsenic(V), tin(IV), and antimony(V) are appreciably soluble in liquid ammonia to give highly colored solutions, but the exact nature

* References are given only to those researches not covered in the Fernelius-Bowman review.

of the reaction in each of these instances has not yet been elucidated (28). Phosphorus(V) sulfide, on the other hand, dissolves in and reacts with liquid ammonia to give a mixture of products which has been identified as the ammonium salts of trithiophosphoric acid and imidodithiophosphoric acid (29).

HALIDES. The behavior of halogen compounds in liquid ammonia parallels the behavior of these same substances in aqueous solution. Ionic halides are recoverable from their solutions in liquid ammonia as such, or in the form of ammoniates. The more covalent the halides become, the greater, however, is the tendency to form either ammonobasic salts or to undergo complete ammonolysis with formation of the ammonium salt and the metal-nitrogen compound. Mercury(II) chloride, tin(IV) iodide, and zirconium iodide form ammonobasic salts. Mercury(II) chloride reacts with ammonia to form ammonobasic mercuric chloride, HgNH_2Cl . This reaction is reversible in that solution in liquid ammonia can be effected by the addition of an excess of ammonium chloride:



The halogen compounds of tungsten, molybdenum, antimony, and uranium also form ammonobasic derivatives, but their exact compositions have not yet been determined.

Typical non-metallic halides undergo vigorous and extensive reaction with liquid ammonia. The halides of phosphorus, germanium, and boron undergo complete ammonolysis to give products that may be looked upon as the ammono acids of these elements. The exact compositions of the substances obtained in each case depend upon the temperature conditions under which ammonolysis is carried out and the treatment which is accorded the products subsequently. The higher the temperature, the greater is the extent of condensation since deammonation takes place in all instances to form eventually products which may be designated as acid anammonides. Such non-metallic nitrides correspond to the oxides of the element.

The extent of ammonolysis is in part dependent upon the formal radius of the positive constituent of the halogen compound, being greater the smaller the radius. Thus, for example, boron trichloride undergoes complete ammonolysis to give boron triamide or diboron triimide; aluminum chloride gives an ammonobasic salt of indefinite composition whereas gallium(III) chloride is soluble in liquid ammonia and recoverable as the ammoniate upon evaporation of the solvent.

Phosphorus(V) oxychloride and sulfuryl chloride, representing examples of typical oxyhalides, undergo ammonolysis with the formation of nitrogen derivatives of phosphoric and sulfuric acids, respectively. In both instances, the resulting products may be regarded as mixed aquo ammono acids. The reactions are not as simple, however, as those presented in Table 17. Only 10 to 15% of the product ob-

TABLE 17

REACTIONS OF INORGANIC HALIDES WITH LIQUID AMMONIA

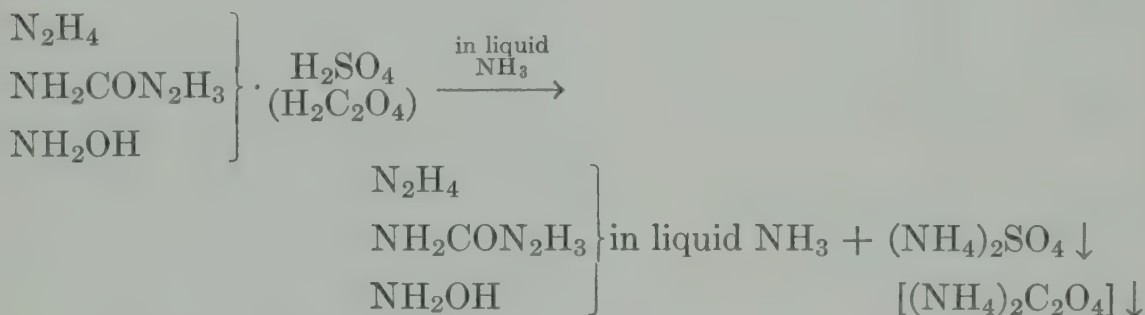
(Arranged on basis of periodic classification)

<i>Reactant</i>	<i>Product</i>	<i>Reactant</i>	<i>Product</i>
HgCl ₂	HgNH ₂ Cl	TiCl ₄	TiNCl·xNH ₃
HgBr ₂	Hg ₂ NBr	TiBr ₄	TiNBr·xNH ₃
HgI ₂	Hg ₂ NI	ZrBr ₄	3Zr(NH) ₂ ·7NH ₄ Br·xNH ₃
BCl ₃	B(NH ₂) ₃	NOCl	NONH ₂
	B ₂ (NH) ₃	PCl ₅	[P(NH)(NH ₂) ₂] _x
B ₂ S ₃	B ₂ S ₃ ·6NH ₃	PNCl ₂	[P(NH)(NH ₂) ₂] _x
AlCl ₃	AlCl ₃ ·xAl(NH ₂) ₃ ?	PCl ₃	P(NH ₂) ₃
		POCl ₃	PO(NH)(NH ₂), PON
CCl ₄	C(NH)(NH ₂) ₂	AsX ₃	As(NH ₂) ₃
SiCl ₄	Si(NH ₂) ₄	SbCl ₃	SbN
	Si(NH)(NH ₂) ₂	VOCl ₃	VO(NH ₂) ₃
	Si(NH) ₂	VCl ₃	V(NH ₃) ₆ Cl ₃
SiH ₃ Cl	(SiH ₃) ₃ N	TaCl ₅	Ta(NH ₂) ₂ Cl ₃ ·3NH ₃
SiH ₂ Cl ₂	[SiH ₂ (NH)] _x		
SiHCl ₃	[SiH(NH)] ₂ NH	TeBr ₄	Te ₃ N ₄
Si ₂ Cl ₆	[Si(NH)NH ₂] ₂	SO ₂ Cl ₂	SO ₂ (NH ₂) ₂
GeCl ₄	Ge(NH) ₂	CrCl ₃	[Cr(NH ₃) ₆]Cl ₃
GeI ₄	Ge(NH) ₂		[Cr(NH ₃) ₅ Cl]Cl ₂
GeI ₂	GeNH	MoCl ₅	Mo(NH) ₂ NH ₂
SnCl ₄	2Sn(NH ₂) ₃ Cl·NH ₄ Cl		

tainable from sulfuryl chloride is actually isolable and identifiable as sulfamide. It is probable that the larger part of the reaction product, in addition to ammonium chloride, consists of a mixture of poly-ammono sulfuric acids. Thiohalides yield derivatives of the thio-ammono acids of the elements.

Table 17, reproduced in part from the Fernelius-Bowman article (24), presents a survey of known reactions between ammonia and various inorganic halides.

PREPARATION OF NITROGEN BASES. An interesting series of replacement reactions involve the preparation of hydrazine, hydroxylamine, semicarbazide (and possibly other nitrogen bases) by the action of liquid ammonia upon the corresponding onium sulfates or oxalates (11). When these salts are brought into contact with liquid ammonia, the free bases are liberated. These are soluble in the solvent, whereas ammonium sulfate (and oxalate) are insoluble. This method has been proposed for the technical preparation of anhydrous hydrazine. It has also been used to prepare ammonia solutions of hydroxylamine and for the isolation of this substance in the crystalline form. Complete interaction is, however, difficult to attain in each of these cases since the individual particles of the reactant are coated by the insoluble ammonium sulfate. If the reaction is carried out at -33°C ., the ammonium sulfate is obtained as a 3-ammoniate, which is exceedingly bulky. It is, nevertheless, possible to remove the precipitated ammonium sulfate by filtration and to evaporate the solution for the recovery of the desired nitrogen bases.



B. AMMONOLYSIS OF ORGANIC COMPOUNDS

HALIDES. Aliphatic halogen compounds undergo ammonolysis with the formation of amines and, in a few instances, quaternary ammonium salts. In so far as the halogen is concerned, the iodides are most easily subjected to solvolysis. However, such reactions are usually rather slow at the boiling point of liquid ammonia, with the result that solutions of organic halogen compounds possess appreciable stability and can, therefore, be used to effect directly alkylation reactions.

The yield of primary amine increases markedly as the radical weight of the organic portion of the halogen compound becomes greater.* Data given in Table 18 indicate that liquid ammonia is superior to alcoholic ammonia where the primary amine is desired.

* There are exceptions to this generalization; thus, for instance, ammonolysis of ethyl iodide yields 46% primary, 31% secondary, and 17% tertiary amine (30).

TABLE 18

ACTION OF LIQUID AMMONIA UPON ALKYL HALIDES

<i>Halogen Compound</i>	<i>Yield of</i>	
	<i>RNH₂</i>	<i>R₂NH</i>
<i>n</i> -amyl bromide	10	80
<i>n</i> -octyl bromide	45	43
<i>n</i> -dodecyl bromide	90	little
benzyl chloride	53	39
	(9) *	(35) *
1-(chloromethyl) naphthalene	72	20
	(11) *	(38) *
β -phenoxyethyl bromide	71
	(65) *

* Percentage yield when ammonolysis is accomplished with alcoholic ammonia.

Halogens substituted on an aromatic ring structure are generally not easily ammonolyzed.

Polyhalogen compounds undergo either ammonolysis to yield the polyamines or dehydrohalogenation. Ethylene dibromide yields principally ethylenediamine together with small quantities of the condensed polyamines. In some instances where ring closure is possible, reaction takes place with the formation of heterocyclic nitrogen derivatives. Thus, for instance, β , β' -dichlorethyl ether will undergo ammonolysis with formation principally of morpholine. Tetrachloroethylene and pentachloroethane undergo dehydrohalogenation.

ALCOHOLS. Many of the low-molecular-weight alcohols are stable in liquid ammonia solution and are also soluble in the solvent. No reaction takes place at the boiling point of liquid ammonia or even at somewhat higher temperatures. If, however, vapor phase reactions are carried out, with such dehydration catalysts being used as alumina and aluminum phosphate, conversion to amines can be made to take place quite readily. There are a few instances, however, where the hydroxyl radical in an organic compound is activated sufficiently so that direct replacement by an amino group can be made to take place in liquid ammonia. Thus hydroxyacetonitrile is converted quite rapidly by treatment with liquid ammonia at room temperatures into aminoacetonitrile.

ALDEHYDES, KETONES, AND RELATED COMPOUNDS. No extensive investigation of the behavior of aldehydes in liquid ammonia has been carried out. There are a few cases of ammonolysis of aldehydes which do not involve the use of liquid ammonia, such as the conversion of

formaldehyde into hexamethylenetetramine. According to Fernelius and Bowman (24) acetals are practically unaffected by liquid ammonia even over long periods of time and in the presence of ammonium salts. This is in contrast to behavior of acetals in aqueous solutions in which they are hydrolyzed quite rapidly by dilute acids.

Some reaction does take place between various ketones and liquid ammonia under rather stringent conditions. Acetophenone when heated with liquid ammonia to 180°C. for 4 hours gives a 3% yield of the corresponding imine. This yield is increased greatly by carrying out the reaction in the presence of ammonobasic aluminum chloride. The mechanism whereby such ammonolysis occurs in the presence of this substance has not been elucidated.

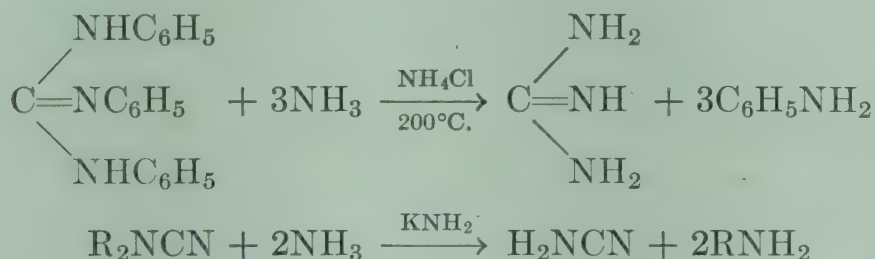
ACIDS, ACID ANHYDRIDES, AND ACID HALIDES. Most of the carboxylic acids are converted into the ammonium salts. At higher temperatures, however, some conversion into the amide is observed to take place. As might be anticipated, acid anhydrides and halides are converted into the corresponding amides.

An interesting series of reactions which are catalyzed by the ammonium ion or by the amide ion has been observed to take place when certain acid amides and related mixed aquo ammono acids are subjected to ammonolysis. Acetamide is partially converted into acetamidine when treated with ammonium chloride in liquid ammonia. Cyanamide, an ammono carbonic acid, is converted into guanidine in the presence of an ammonium salt. No conversion is observed to take place in the absence of the ammonium salt, although polymerization of cyanamide can be effected under these conditions. The conversion of ammonium carbamate into urea as practiced technically requires operation at high pressures and temperatures and conceivably also involves an acid-catalyzed ammonolytic reaction. It is exceedingly difficult to replace the carbonyl oxygen in urea by an NH group; however, 30% yields of guanidine are obtainable when urea and ammonia in the presence of ammonium nitrate (1:1:1 mole ratio) are heated at a temperature of 300°C. for 16 hours (31).

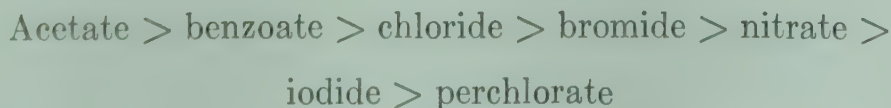
ESTERS. Many esters undergo ammonolysis when treated with liquid ammonia at -33°C.; reactions take place more rapidly when such mixtures are heated to higher temperatures. The extent of ammonolysis is definitely dependent upon the nature of the ester. For instance, ethyl esters of formic, acetic, propionic, valeric, caprylic, and phenylacetic acid undergo no appreciable reaction when allowed to stand with liquid ammonia at -33°C. for a period of as long as 24 hours. The ethyl esters of mono-, di-, and trichloroacetic acid give quantitative yields of corresponding amides under the same conditions.

Ethyl oxalate is rapidly and completely converted into oxamide. Ethyl malonate also undergoes ammonolysis quite rapidly. Ethyl carbonate is ammonolyzed to both urea and guanidine when heated at 300°C. for 64 hours with a solution of ammonium chloride.

Ammonium salts and soluble metallic amides have been found to catalyze the ammonolysis of esters, just as acids and bases bring about more rapid hydrolysis. It has been observed that triphenylguanidine, which may be regarded as the triphenyl ester of an ammono carbonic acid, can be converted into guanidine and aniline by heating with ammonia at 200°C. in the presence of ammonium chloride. No reaction is observed in the absence of the ammonium salt. It has also been shown that alkyl cyanamides react with potassium amide in liquid ammonia to yield the corresponding amines and potassium cyanamide, where the alkyl group is ethyl, *n*-propyl, and isobutyl.



Concurrent investigations were begun about 1935 by Shatenshtein in Russia and Audrieth and co-workers in this country to determine the catalytic effect of ammonium salts on the ammonolysis of various esters and ester-like materials. In so far as lactones represent inner esters, Shatenshtein was able to prove that conversion of santonin into the corresponding amide takes place much more rapidly in the presence of substances which act as acids in liquid ammonia. The reaction of santonin with liquid ammonia was found to be autocatalytic in nature because of the formation of the acid amide, which behaves as an acid in liquid ammonia. Addition of the reaction product to the lactone-ammonia mixture causes the induction period observed during the ammonolysis to disappear. Urea and phenol were also found to catalyze this reaction. The catalytic effect of ammonium salts was found to be much more profound; rate of conversion into the amide is definitely a function of concentration of the catalyst. Using equimolar concentrations of various ammonium salts, the Russian investigators found the catalytic effect to decrease in the following order:



This order of catalytic activity is, however, the reverse of the presumed order of acid strengths of the corresponding ammonium salts based on physical and conductance studies. In commenting on these experimental findings, Shatenshtein pointed out: (a) that strong acids apparently become weaker in ammonia whereas weak acids become stronger because of the high proton affinity of the solvent (leveling effect); and (b), since ammonia is a solvent of low dielectric constant, appreciable interionic forces come into play, with the result that the stoichiometric concentrations of the ammonium salts do not reflect the actual concentrations of available ammonium ion.

Diethyl malonate was the first of the esters to be studied by American investigators. Ammonolysis in this instance was also found to be autocatalytic in nature; such autocatalytic behavior was found to disappear when ammonium salts are added to speed up the reaction. The catalytic effect of added ammonium salts is definitely apparent from the figures given in Table 19, in which are noted the times re-

TABLE 19

AMMONOLYSIS OF ETHYL BENZOATE

(Moles $\text{C}_6\text{H}_5\text{COOC}_2\text{H}_5 = 0.035$; moles $\text{NH}_3 = 0.82 \pm 0.03$)

<i>Catalyst</i>	<i>Mole Catalyst Used</i>	<i>Temper- ature, °C.</i>	<i>Reaction Velocity Constant</i>	<i>Half Time of Reaction, in Hours</i>
None	25	0.00014	~5000
NH_4Cl	0.00935	0	0.000786	882
NH_4Cl	0.00935	25	0.00272	255
NH_4Cl	0.01870	0	0.00160	433
NH_4Cl	0.01870	25	0.00576	120
NH_4Br	0.00935	25	0.00208	333
NH_4ClO_4	0.00935	25	0.00155	447
$\text{C}_6\text{H}_5\text{COONH}_4$	0.00935	25	0.00336	206

quired for 50% conversion of ethyl benzoate into benzamide. Here again the catalytic effect of equivalent concentrations of various ammonium salts is opposite to what might be expected from a consideration of the physical properties of solutions of these "acids" in liquid ammonia.* Increase in the concentration of the added ammonium salt brings about proportional acceleration in the speed of the reaction.

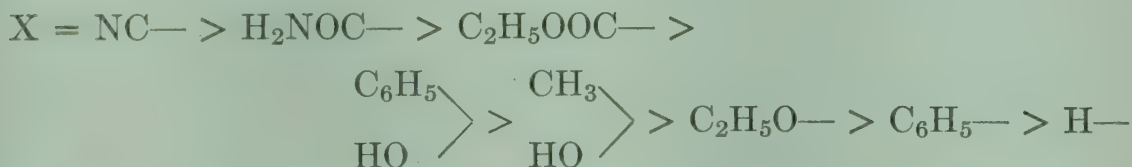
The ammonolysis of fats and oils both at room temperatures and under pressure at 165°C . is also markedly accelerated by addition of ammonium salts (34). Soybean oil, olive oil, tung oil, linseed oil.

* This unexpected order of catalytic activity of onium salts holds also for aminolytic reactions in such solvents as *n*-butylamine and cyclohexylamine (32, 33).

cottonseed oil, castor oil, and even pork lard are readily converted into amides of the corresponding fatty acids.

It was later observed that the sodium salts corresponding to the ammonium salts which had been employed in these studies are also capable of exerting a catalytic effect. Other electrolytes, on an equimolar basis, are not as effective as the ammonium salts. There is no question, however, but that their presence greatly accelerates such reactions. Even though ammonium salts have been found to catalyze markedly the ammonolysis of esters, as was anticipated on the basis of analogy, it can now definitely be stated that the findings with respect to so-called acid catalysis in liquid ammonia presumably represent special cases of what might more properly be regarded as examples of electrolyte catalysis (35).*

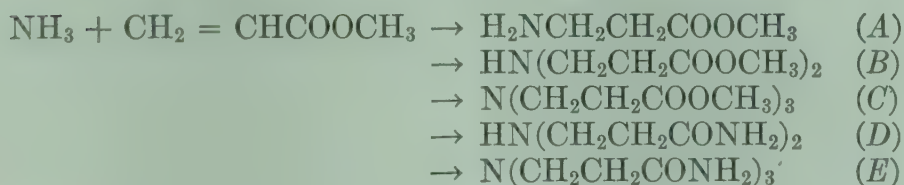
The effect of α -substituents on the rate of ammonolysis of esters parallels very closely the activating effect which is observed when saponification of these same substances is carried out. The influence of the α -substituents in esters of the type XCH_2COOR is given by the following series, where



Esters of unsaturated acids react with ammonia both by addition to the double bond as well as by ammonolysis. Ammonation of methyl

TABLE 20

AMMONOLYSIS OF METHYL ACRYLATE IN LIQUID AMMONIA AT ROOM TEMPERATURE



Yield (percentage)

<i>Time</i>	<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>	<i>E</i>
100 hours	2.5	42	15.5
14 days	~35	~13
5 months	~33	~56

* Independent experimental evidence in support of this point of view has been presented by Watt (36, 37, 38) and his students, who have studied the ammonolysis of organic halides. In certain cases the catalysis exhibited by ordinary salts is even more pronounced than that obtained with ammonium salts.

acrylate is found to occur more rapidly than ammonolysis giving the amino, imino, and nitrido propionic acid derivatives. Ammonolysis of the alkoxy group to produce the corresponding amides occurs more slowly, as indicated from the data given in Table 20.

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METAL-AMMONIA SOLUTIONS

Weyl (1) was the first to observe (in 1864) that sodium and potassium are soluble in liquid ammonia. He postulated that such solutions could be regarded as combinations of metal with ammonia and called them "metal ammoniums." Seely (2) subsequently confirmed the observations recorded by Weyl, but came to the conclusion that such solutions are true solutions, since removal of the ammonia by evaporation reforms the metal without apparent decomposition. No effort was made to use such metal-ammonia solutions for reduction reactions until the French chemist, Joannis, undertook a series of investigations which were published in *Comptes rendus* between 1889 and 1894. Joannis also considered sodium solutions in ammonia to constitute "metal ammonium" combinations. This concept was generally accepted until the more precise physicochemical investigations of these systems were begun by Ruff and Geisel (3) in Germany and Kraus (4) in this country.

All the alkali metals as well as the alkaline earth elements are soluble in liquid ammonia. Magnesium is also slightly soluble (5). McElroy, Kleinberg, and Davidson (6) have been able recently to demonstrate that solutions of metallic aluminum may be prepared by electrochemical methods.

The solutions of alkali and alkaline earth metals, magnesium, and aluminum all possess a characteristic deep blue color in the dilute concentration ranges; the more soluble alkali metals impart a coppery-bronze color to saturated solutions. The absorption spectra of the blue solutions of the alkali and alkaline earth metals are in all cases the same, indicating that some common component in such systems is responsible for their color. The metal-ammonia solutions may be prepared either by dissolving the metals directly in liquid ammonia or electrochemically by discharge at the cathode, in which case the blue color develops in the cathode region. The very early observation by Palmaer (7) that electrolysis of solutions of tetraalkylated ammonium salts leads to the development of a blue color at the cathode

raised hopes that some of these radicals would be found capable of existence in the free state.

The metal-ammonia solutions possess varying stability. Solutions of sodium in liquid ammonia have been kept for months, even at room temperature, without appreciable decomposition. Solutions of the more active alkali metals such as rubidium and cesium undergo more rapid reaction with the solvent and are eventually converted into the colorless solutions of the corresponding amides. There are a good many substances which catalyze the conversion of the metal-ammonia solutions into the corresponding amides. Active metals such as iron, cobalt, and nickel are particularly efficient catalysts. The greater stability of such metal-ammonia solutions as contrasted with the great reactivity of these elements towards water is probably due to the fact that ammonia undergoes self-ionization only to a very limited extent. The ion-product constant is of the order of 10^{-33} as compared with a value of 10^{-14} for water. This negligible self-ionization of ammonia is responsible for many of the distinctive properties and reactions of the solvent, including stability of the very active metals which dissolve therein.

When the blue solutions of the alkali elements are evaporated, the metal is obtained; but in the case of the alkaline earth metals there are formed crystalline ammoniates, $M(NH_3)_6$, which appear to be coordination compounds of the respective elements with ammonia. Deammonation of these products is accompanied by appreciable decomposition to give the corresponding amides or nitrides.

It was Hamilton P. Cady (8) who first observed in 1897 that solutions of sodium in liquid ammonia are extraordinarily good conductors. Electrical properties of sodium solutions in liquid ammonia were subsequently studied in detail by Kraus (4, 9), who found that the equivalent conductance of such solutions at all concentrations is greater than for any known salt in any known solvent. The conductivity is also extremely high in concentrated solutions approximating values for the metals, as is evident from the following data:

	<i>Specific Conductivity, κ</i>
Saturated solution of sodium in liquid ammonia at -33.5°C .	0.5047×10^4
Saturated solution of potassium in liquid ammonia at -33.5°C .	0.4569×10^4
Mercury at room temperature	1.063×10^4

Conductance values pass through a minimum but then increase again with dilution (see Figure 12). Conductance of such metal-ammonia solutions is metal-like in concentrated solutions, but electro-

lytic in character in the dilute range. These observations led Kraus to propose that solutions of sodium in liquid ammonia in the concentrated range consist largely of sodium ions and free electrons, which

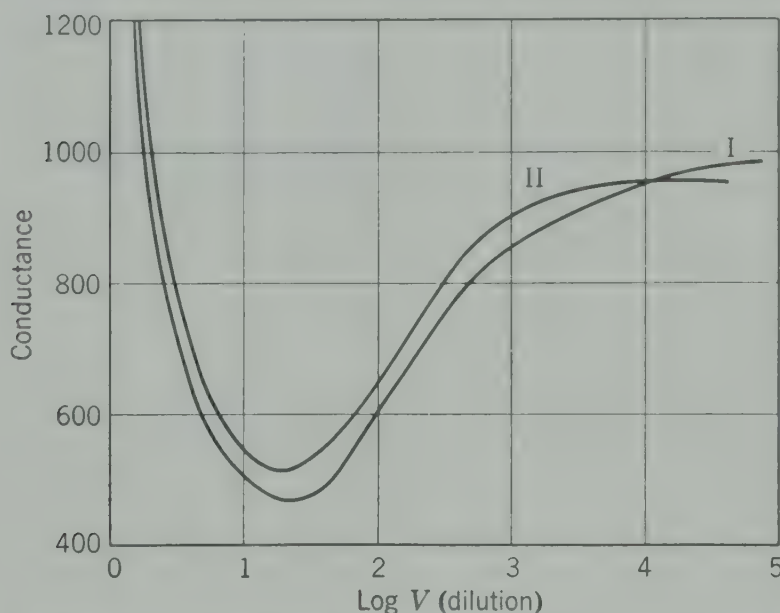


FIGURE 12. The conductivities of solutions of sodium(I) and of potassium(II) in liquid ammonia at -33°C .

are not greatly inhibited by the presence of the solvent. In the more dilute ranges, however, with increase in solvent concentration, electrons become solvated. The current carriers, under these conditions, are the alkali metal ions and solvated electrons. Data for the conductance of sodium in liquid ammonia at -33.5°C . are given in Table 21.

TABLE 21

CONDUCTANCE OF SOLUTIONS OF SODIUM IN LIQUID AMMONIA AT -33.5°C .

<i>V (Dilution in Liters)</i>	<i>Λ (Equivalent Conductance)</i>
0.5047	82490
0.7861	12350
1.038	3228
2.798	749.4
6.305	554.7
30.40	478.5
65.60	540.3
690.1	869.4
3479.0	988.6
17260.0	1016.0
37880.0	1034.0
∞	1040.0

The ionic conductance value for the sodium ion (for all sodium salts in liquid ammonia at this temperature) has been given as 130, which means that the conductance value for the negative carrier must be around 900 to 910. Even though ammonia is a solvent of low viscosity, thus permitting charged particles to migrate at higher mobilities, it is obvious that the negative particle which accounts for this extraordinarily high conductance must be very, very small compared with any other negative ion. Kraus came to the conclusion that the negative particle is the solvated electron. Although his concept is not completely in agreement with all the facts that are now known, it is significant that the theory proposed by him in 1907 is still the most rational one that has been offered. Pertinent quotations from his original articles follow.

"These solutions, therefore, constitute a connecting link between metallic and electrolytic conductors. In dilute solutions the process is, at least in part, electrolytic. A portion of the current is carried by the positive carriers as they appear in solutions of the common salts. The negative carrier is chemically uncombined, but is associated with one or more molecules of the solvent. These carriers are identical for solutions of all metals, and, when the discharge occurs at the anode, the only material process which takes place is that a portion of the solvent is left behind in the immediate neighborhood of this electrode. As the concentration of the solution increases, the nature of the phenomenon changes only in so far as the combination of the negative carrier with ammonia is affected. At the higher concentrations, the negative carriers are free from association with the ammonia molecules to a greater and greater extent. And, since under these conditions the negative carrier is associated with no matter of atomic dimensions, it follows that all the material effects cease so far as these carriers are concerned. It is not to be understood that a given carrier is free from association with the solvent molecules for any considerable period of time. Obviously, an equilibrium must exist between the free carriers and the combined carriers and ammonia, which results in a constant interchange between the free and bound carriers. During the interval over which these carriers are free from the solvent molecules, they conduct just as they do in metals. As the concentration is further increased, the number of free carriers constantly increases. It is evident that their number in the more dilute solution, for example, in the neighborhood of normal, must be relatively small, since at the higher concentrations the equivalent conductance reaches values some one hundred times as great as that at normal concentra-

tion. It is not possible to determine the actual number of carriers in the more concentrated solutions. In the more dilute solutions, however, it appears that the number of carriers decreases with increasing concentration just as it does in the case of normal electrolytes in ammonia.

"There is nothing to distinguish the more concentrated solutions from actual metallic substances. It may be concluded, therefore, that the process of conduction in the case of ordinary metals is effected by means of the same negative carrier. Since this carrier is negatively charged and has sub-atomic dimensions, we may conclude that it is identical with the negative electron as it appears in radioactive and other phenomena."

The alkali metal solutions in liquid ammonia are unusual in many other respects. Despite the fact that high mobility would indicate very small size on the part of the negative carrier, it was Johnson (10) who pointed out in 1931 that saturated solutions of sodium and of potassium in liquid ammonia are among the lightest known liquids. The density of liquid ammonia at -33.8°C . is 0.6824 gram per cc. The density of a saturated sodium solution is 0.54 gram per cc., and that of a saturated potassium solution is 0.63 gram per cc. Since the saturated solution of sodium in liquid ammonia contains approximately one gram-atom of sodium per 5.5 moles of ammonia, the theoretical volume of such a solution should amount to about 158 cc. The actual volume is well above this figure, about 210 cc. No such abnormalities have been observed for solutions of salts in liquid ammonia. Johnson has said:

"The increase in volume noted in the case of the metal solutions cannot be attributed to the metal ions. It must be due to the negative constituent, the electron associated with the solvent molecules. The envelope of ammonia molecules associated with the electron must possess a considerable volume to account for these results (10)."

Although a tremendous amount of work has been done to elucidate the physical nature of such solutions, it is still significant that the exact status of electrons in metal-ammonia solutions remains an unsolved problem.* Emphasis is placed in the discussion which follows upon the usefulness of metal-ammonia solutions. Several excellent review articles covering the chemical properties of such systems have

* It is suggested that readers consult references 9 and 11-14 for more detailed information about the physics and physical chemistry of metal-ammonia solutions.

been published by Watt (15, 16). The statements which follow are quotations from these articles:

"The unique properties of the liquid ammonia solutions of the alkali and alkaline earth metals present unusual opportunities for the study of reduction reactions. Although liquid ammonia is somewhat selective and limited in the solvent action toward inorganic substances, many electrolytes exhibit high solubility and many others participate in oxidation-reduction reactions even though they are substantially insoluble."

Ammonia is, however, a much better solvent for organic compounds. It is in the field of organic chemistry that such solutions find greatest application both in synthesis and for the study of reduction reactions. "By comparison with water as a medium for the study of reactions of strong reducing agents, ammonia possesses certain distinct advantages," Watt says, and then goes on to state that "the utility of water is seriously limited by the fact that reducing agents stronger than hydrogen liberate hydrogen from water." He continues: "Ammonia, on the other hand, permits of the study of the extremely strong reducing systems provided by solutions of the alkali and alkaline earth metals over a wide range of concentration and temperature. An additional advantage is a consequence of the relatively low degree of autoionization of ammonia."

It is only fair to state that there are some objections to the use of metal-ammonia solutions. More elaborate equipment is needed. Reactions must be carried out at lower temperatures or under pressure. Ammonia is a somewhat hygroscopic liquid and also absorbs carbon dioxide; its use, therefore, requires more care than need normally be given to the common solvents.

Reduction by means of solutions of metals in ammonia consists in addition of one or more electrons to an atom, a group of atoms, or an ion. In effect, therefore, solutions of the alkali and alkaline earth metals in ammonia are powerful reducing agents because they represent media in which the electrons are more readily available for reaction than in any other system. The metal ion in these instances rarely exerts a specific effect.

The presentation of experimental observations is taken largely from the two comprehensive articles covering reactions of metal-ammonia solutions published by Watt (15, 16). These articles should be consulted for more specific details and original references. Inorganic reactions are covered first, followed by a discussion of the reduction of organic compounds. Reduction can be accomplished either by elec-

tron addition or by active (nascent) hydrogen. In the latter instance the reaction between the metal-ammonia solution and the compound is permitted to take place in the presence of some material which acts as an acid in liquid ammonia such as ammonium salts, alcohols, phenols, yes, and even water!

REDUCTION OF INORGANIC SUBSTANCES (15)

ELEMENTS. It is not surprising to find that a great many elements will undergo direct reaction with metal-ammonia solutions. The elements which are reduced under such circumstances consist largely of the representative elements, that is, those whose atomic numbers are two to four units less than those of the inert gases. A survey is presented in Table 22 of some of the experimental observations having to do with reactions of sodium, potassium, and in a few instances calcium, with such elements as germanium, tin, lead, arsenic, antimony, bismuth, phosphorus, oxygen, sulfur, selenium, and tellurium. The first step in all these reactions is the formation of a normal binary compound which is generally only slightly soluble in liquid ammonia. These compounds then react with an excess of the indicated elements to form soluble homopolyatomic anionic complexes.

Thus, for example, sulfur will react with a solution of sodium in liquid ammonia to yield initially a precipitate of sodium sulfide. This precipitate reacts with an excess of sulfur to give a series of polysulfides, Na_2S_x , in which x may be as great as 7. Selenium gives first the slightly soluble normal salt, sodium selenide, Na_2Se . The latter reacts with an excess of selenium to give successively the bright-red solution of the diselenide, the wine-red solution of the triselenide, then the green solution of the tetraselenide, and finally red-green solutions in which the species Na_2Se_5 and Na_2Se_6 are present.

Lead dissolves in a solution of sodium in liquid ammonia to give a green solution of the normal plumbide, which is capable of dissolving additional lead eventually to form a product that can be represented by the formula Na_4Pb_9 . Evaporation of the green solution of Na_4Pb_9 gives at low temperature a crystalline salt-like material which is converted at temperatures in the neighborhood of 0°C . into an intermetallic phase containing no ammonia. Solutions of this polyplumbide are colloidal in character and exhibit the Tyndall effect. If such a solution is electrolyzed, 2.26 gram-atoms of lead per Faraday is discharged at the anode as might be expected for a Pb_9^{-4} ion. If the sodium polyplumbide solution is treated with a solution of a lead salt, an ionic re-

TABLE 22

REACTIONS OF METAL-AMMONIA SOLUTIONS WITH ELEMENTS

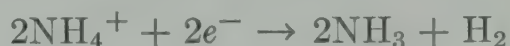
<i>Element</i>	<i>Metal- Ammonia Solution</i>	<i>Products</i>
Pb	Li	Li_4Pb_x
	Na	$\text{Na}_4\text{Pb} \cdot 2\text{NH}_3$, NaPb , NaPb_2 , Na_4Pb_9
	K	$\text{K}_4\text{Pb}_9 \cdot x\text{NH}_3$
P	Na	$\text{NaP}_3 \cdot 3\text{NH}_3$
	K	$\text{KP}_5 \cdot 3\text{NH}_3$
As	Li(Na)	$\text{Li}_3\text{As}(\text{Na}_3\text{As})$
	K	K_3As , K_2As_4
Sb	Li	Li_3Sb
	Na	Na_3Sb , $\text{Na}_3\text{Sb}_{5-7}$
Bi	Na	Na_3Bi , Na_3Bi_3 , $\text{Na}_3\text{Bi}_{5-7}$
O_2	Li	Li_2O , Li_2O_2 , $\text{LiO}_2(?)$
	Na	$(\text{NaOH}, \text{NaNH}_2, \text{NaNO}_2)$ Na_2O , Na_2O_2 , $\text{NaO}_{1.67}$ (or $4\text{NaO}_2 \cdot \text{Na}_2\text{O}_2$)
	K	K_2O_2 , KO_2
	Rb	Rb_2O , Rb_2O_2 , RbO_2
	Cs	Cs_2O , Cs_2O_2 , Cs_2O_3 , CsO_2
	Ba	BaO , BaO_2
	Li	Li_2S , Li_2S_2 , Li_2S_3 , Li_2S_4 , Li_2S_x
	Na	Na_2S , Na_2S_2 to Na_2S_7 , and Na_2S_x
	K	K_2S , K_2S_2 to K_2S_5 , and K_2S_x
	Rb(Cs)	$\text{Rb}_2\text{S}(\text{Cs}_2\text{S})$
Se	Ca	CaS and CaS_x
	Li	Li_2Se , Li_2Se_2 to Li_2Se_5
	Na	Na_2Se , Na_2Se_2 to Na_2Se_6
	K	K_2Se , K_2Se_2 to K_2Se_4 , and K_2Se_x
Te	Rb(Cs)	$\text{Rb}_2\text{Se}(\text{Cs}_2\text{Se})$
	Na	Na_2Te , Na_2Te_2 , Na_2Te_3 , $\text{Na}_2\text{Te}_4(?)$
	K	K_2Te , K_2Te_3
	Rb(Cs)	$\text{Rb}_2\text{Te}(\text{Cs}_2\text{Te})$

action takes place which may be represented by the equation $\text{Pb}_9^{-4} + 2\text{Pb}^{++} \rightarrow \text{Pb}_2\text{Pb}_9$. The resulting product is, however, no different from ordinary lead.

The reactions of oxygen with solutions of alkali metals in liquid ammonia are extremely interesting. The first step in the slow oxidation of sodium involves the formation of sodium oxide, which is relatively insoluble and on standing undergoes ammonolysis to give a mixture of sodium hydroxide and sodium amide. The rapid oxidation under special conditions results in the formation of a compound with the empirical formula $\text{NaO}_{1.67}$, which corresponds to a combination of 4 NaO_2 to 1 Na_2O_2 . Attempts to convert sodium completely to NaO_2

were not successful in liquid ammonia. It is only under high oxygen pressure and at higher temperatures that sodium absorbs sufficient oxygen to give the superoxide NaO_2 . Compounds corresponding to the superoxide can, however, be obtained in liquid ammonia from the larger alkali metals such as potassium, rubidium, and cesium. The reactions of oxygen with the alkali and alkaline earth metals in liquid ammonia, and at higher temperatures, have recently been the subject of extensive studies by Kleinberg and co-workers (17, 18, 19).

AMMONIUM SALTS AND HYDRIDES. Reference has already been made to the fact that ammonium salts constitute the acids of the ammonia system. If such acids are not reducible per se, they are converted by treatment with metal-ammonia solutions into the corresponding metal salts with the evolution of hydrogen:



This procedure has been utilized as a means for determining the extent of reduction of both inorganic and organic compounds. The substance under investigation is treated with an excess of the alkali or alkaline earth metal solution in liquid ammonia, and the excess is then determined by titrating with solid ammonium chloride or ammonium bromide to the disappearance of the blue color. The quantity of metal used to effect the reduction of a compound can thus be determined accurately. Alternatively, an ammonium salt solution is added, and the excess of metal-ammonia solution is determined from the volume of hydrogen evolved. The apparatus depicted on page 73 in Chapter 5 has been employed for this particular purpose.

Solutions of ammonium salts containing non-reducible anions are converted by metal-ammonia solutions into the corresponding metal salts. This is true of the ammonium halides, ammonium azide, ammonium cyanide, ammonium sulfide, ammonium acetate, and ammonium perchlorate. Ammonium salts with oxidizing radicals such as the chromate and dichromate and the nitrate suffer reduction in which the oxidizing anion is affected by metal-ammonia solutions.

In some instances, ammonium salts of ammono acids behave differently in ammonia than in aqueous solutions. Sulfamic acid is a monobasic acid in water. In liquid ammonia, however, two equivalents of sodium per mole of sulfamic acid undergo reaction, indicating that sulfamic acid is actually a dibasic ammono sulfuric acid. The more basic nature of liquid ammonia also permits the development of acidic character on the part of hydrides which do not react as acids in more acidic media. Thus, for instance, diborane is quite soluble in liquid ammonia. A diammoniate may be obtained from such a solution.

Treatment of the solution of diborane in liquid ammonia with sodium results initially in the rapid evolution of one-half mole of hydrogen per mole of diborane. Solutions of diborane which have been allowed to remain in contact with liquid ammonia before the sodium is added do, however, liberate more hydrogen than that corresponding to the equation given below, indicating that the diammoniate of diborane presumably behaves as a dibasic acid:



The simple hydrides of germanium, arsenic, and phosphorus, GeH_4 , AsH_3 , and PH_3 , react to give monosodium derivatives which are fairly soluble in liquid ammonia. Such alkali metal compounds can be subjected to alkylation directly in liquid ammonia to give the mono-alkyl derivatives (20). There are distinct advantages to this synthetic approach since the lower alkyl halides are quite soluble in liquid ammonia and react with the sodium derivatives by what may be considered to be an ionic mechanism as indicated below:



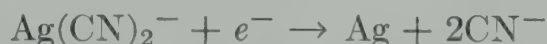
Even water reacts with metal-ammonia solutions to give the insoluble hydroxides. Traces of water can thus be determined quite readily. Dehydration to effect production of absolutely anhydrous ammonia can be accomplished by distilling ammonia from a metal-ammonia solution.

METAL HALIDES. Metallic halides react with metal solutions of liquid ammonia to give (a) free metals, (b) intermetallic compounds, or (c) homopolyatomic anionic compounds containing the reduced metals. Thus, for instance, solutions of copper, silver, and gold compounds are usually reduced to the free metals in liquid ammonia by metal solutions. Iron, nickel, and cobalt salts are also reduced to the metals, but, in each of these instances, the product metal catalyzes subsequent reaction of unchanged metal-ammonia solution to give the amides or amphoteric amides of the metal involved. The halides (and cyanides) of zinc, cadmium, mercury, and thallium react to give insoluble intermetallic compounds whose compositions vary with the nature of the alkali and/or alkaline earth-metal ammonia solutions. Such compounds as NaZn_4 , Ca_7Zn , NaCd , NaCd_{5-7} , Ca_3Hg_2 , NaHg , Na_3Tl_2 , NaTl , and NaTl_2 have actually been isolated and identified. Halides of elements which tend to form homopolyatomic anionic com-

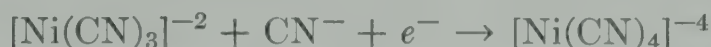
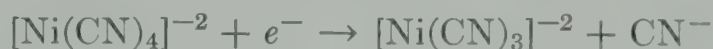
plexes yield these on treatment with metal-ammonia solutions, for example, lead, tin, antimony, and bismuth halides.

OXIDES. The primary reduction product of oxides of the normal elements with solutions of potassium appears to be the free element. The latter may then form a soluble or insoluble intermetallic compound with the excess of alkali metal. Reactions of this sort occur with bismuth(III) oxide, arsenic(III) oxide, tin(II and IV) oxides, lead(II and IV) oxides, zinc oxide, and cadmium oxide. Oxides of the transition elements may be reduced to the elemental state; in most instances, however, some intermediate lower oxide is obtained. This is true of molybdenum(VI) oxide, which is reduced quantitatively to molybdenum(III) oxide when three equivalents of a potassium-ammonia solution are employed. If a larger amount of potassium is used, the reduction gives mixtures of the molybdenum(III) oxide and the element.

COMPLEX CYANIDES. The simple cyanides behave in many instances like the halides. The complex cyanides, on the other hand, vary distinctly in their behavior. The complex cyanides of copper, silver, zinc, and cadmium are reduced to the free metals by a reaction which can be illustrated by the following equation:



The complex nickel(II) [and palladium(II)] cyanide undergoes step-wise reduction in accordance with the following equations:



In the case of nickel, there is definite evidence for the formation of a nickel(I) compound with the formula $\text{K}_2\text{Ni}(\text{CN})_3$. The end product is a nickel(0) complex. Watt has pointed out that "the central atom of the complex nickel(0) ion exhibits an effective atomic number equal to the atomic number of the inert gas at the end of the period in which the element is placed in the periodic classification. . . . These complex ions are comparable to the known carbonyl of nickel, $\text{Ni}(\text{CO})_4$, and the anticipated carbonyl of palladium." Since the cyanide ion possesses a negative charge even though structurally similar to the carbon monoxide molecule, a corresponding number of positive ions must be present to balance the charge on the negative ion.

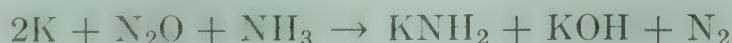
REDUCTION OF MISCELLANEOUS INORGANIC COMPOUNDS. One of the most interesting observations involves the reduction of sodium nitrite with metallic sodium, resulting in the formation of an orange precipi-

tate whose composition corresponds to the formula Na_2NO_2 . This product, although extremely explosive, has been studied by many workers. It is obtainable in many instances where nitrates or nitrites of the elements are reduced by some alkali metal in liquid ammonia. Thus, for instance, the reaction of metallic potassium with ammonium nitrate results in the formation of this particular product together with other contaminants. The compound Na_2NO_2 has been called sodium hydronitrite, the salt of hyponitrous acid. It is soluble in solutions of ammonium salts in liquid ammonia but apparently undergoes decomposition under these circumstances. Hydroxylamine, hyponitrite, and other substances as yet to be identified are found among the decomposition products (21).

Such materials as potassium permanganate and sodium bromate undergo rather complicated reduction reactions with the alkali metals in liquid ammonia. Silver cyanate is unaffected by metallic sodium except that the positive silver ion is reduced and precipitated as the metal; the cyanate ion itself does not appear to be affected. On the other hand, the cyanate is partially reduced to cyanide when metallic calcium is employed as reductant. The thiocyanate ion is apparently also more actively affected by metallic calcium than by the alkali metals.

A number of very interesting reactions have been carried out involving the action of gases of simple molecular composition upon solutions of the alkali and alkaline earth metals in liquid ammonia. Carbon monoxide is absorbed by alkali metal solutions in a 1:1 molar basis. This has led to the assumption that alkali metal carbonyls are formed. It is doubtful whether this explanation is correct, however. Nitric oxide reacts with metal solutions to give metal nitrosyls, $(\text{MNO})_x$. These substances dissolve and react in water with the evolution of nitrous oxide and the formation of a solution which contains the hyponitrite ion. It seems clear, however, that the initial reaction of nitric oxide with sodium or potassium in liquid ammonia does not immediately give hyponitrite. Nitrogen dioxide is also reduced by metal-ammonia solutions to give products similar to those obtained from nitric oxide.

The reaction between a potassium-ammonia solution and nitrous oxide is much more complicated. The first step undoubtedly involves formation of potassium amide, which is soluble in liquid ammonia, precipitation of potassium hydroxide, and liberation of nitrogen in accordance with the following equation:



Nitrous oxide then reacts with potassium amide to form the corresponding azide by a reaction similar to the high-temperature process which was at one time used for the commercial production of the alkali metal azides:



It is interesting to note that this particular reaction is now carried out in liquid ammonia, essentially in accordance with the equation given above, for the commercial production of sodium azide.

ORGANIC REACTIONS (16)

There is available a tremendous amount of information covering reactions of organic and organometallic compounds with metal-ammonia solutions. It is significant, however, that most of this information is qualitative in character. As usual, the objective in such studies has been the isolation of some one particular end product; little or no attention has been paid to side reactions or to reaction mechanisms.

It should again be emphasized that two distinct types of reactions are possible involving the action of metal-ammonia solutions upon organic compounds. Not only can the electron serve as the reducing agent, that is, reduction be effected by what amounts to the metal-ammonia solution itself, but advantage can also be taken of the fact that such metal-ammonia solutions react readily with acidic substances in liquid ammonia such as the ammonium salts, alcohols, phenols, and water to form active (nascent) hydrogen in situ. Processes of the latter type amount to hydrogenation reactions, as contrasted with the electron reduction mechanisms which are most common among inorganic compounds.

The reactions which may take place involving organic compounds and metal-ammonia solutions have been classified by Watt as follows:

A. Displacement of an equilibrium involving an organic compound, the solvent and an ammonium salt. Whenever a substance is ammonolyzed to form even a small quantity of ammonium salt, the resulting equilibrium can be displaced by removal of the ammonium ion through reaction with the metal-ammonia solution:



B. Displacement reactions. The basic nature of ammonia as a solvent accentuates the tendency for many organic compounds to dissoci-

ate the proton. Reaction thus leads to the formation of the metal salt and the displacement of hydrogen. It should be recognized, however, that the hydrogen which is formed may itself bring about reduction and/or hydrogenation of the organic molecule:



C. Metal addition. There are numerous instances where compounds containing double or triple bonds undergo reduction by electron addition with the formation of the metal salts. Such reactions are known for compounds containing the following groups: $\text{C}=\text{C}$, $\text{C}\equiv\text{C}$, $\text{C}=\text{O}$, $\text{C}=\text{N}$, $\text{N}=\text{O}$ and $\text{N}=\text{N}$. Free radicals (or the dimers thereof) also undergo electron addition with formation of the ions; for example, R_3C , R_3Si and R_3Ge are thus converted into the metal compounds.

D. Bond rupture. Bond rupture may occur when the following linkages undergo reaction: $\text{C}-\text{C}$, $\text{Si}-\text{Si}(?)$, $\text{Ge}-\text{Ge}$, $\text{Sn}-\text{Sn}$, $\text{Pb}-\text{Pb}$, $\text{C}-\text{Sn}$, $\text{C}-\text{Pb}$, $\text{Si}-\text{Ge}$, $\text{Si}-\text{Sn}$, $\text{C}-\text{O}$, $\text{Ge}-\text{O}$, $\text{Sn}-\text{O}$, $\text{C}-\text{N}$, $\text{C}-\text{Bi}$, $\text{Sn}-\text{N}$, $\text{S}-\text{S}$, $\text{N}-\text{N}$, $\text{C}-\text{S}$, $\text{C}-\text{Hg}$, and $\text{C}-\text{X}$ (where X is a halogen).

E. Removal of halogen. Actually the removal of halogen involves bond rupture between a carbon and a halogen atom. The halogen always appears as the halide ion; the organic radical or group may appear as such, may undergo dimerization, or ammonolysis, or be converted into the corresponding ion, according to the following series of reactions:



F. Removal of other elements. Reduction of nitro groups proceeds through a first step in which oxygen is removed with the formation of sodium oxide, which is then subsequently ammonolyzed to a mixture of sodium hydroxide and sodium amide.

HYDROCARBONS. The nature of the reaction which takes place when hydrocarbons are subjected to the action of metal-ammonia solutions depends upon one or more of the following considerations:

A. If the hydrocarbon contains a labile hydrogen atom, replacement by metal may take place.

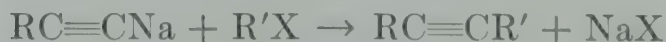
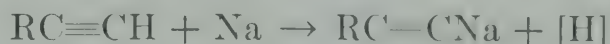
B. If the hydrocarbon is unsaturated, reduction through hydrogenation may occur.

C. The reduction and hydrogenation referred to in *B* above may even occur in those instances where the hydrocarbon itself undergoes no reaction with the metal-ammonia solution, provided there is present some reagent such as water, alcohol, or an ammonium salt which reacts with the metal-ammonia solution to yield active hydrogen.

The saturated aliphatic hydrocarbons do not react with metal-ammonia solutions. When aryl substituents are introduced, acidic character develops, and reaction takes place with the formation of the alkali metal salts. Thus, for instance, triphenylmethane reacts to give the triphenylmethide and hydrogen.

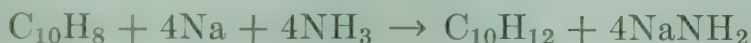
The ethylenic hydrocarbons are not particularly reactive towards solutions of metals in liquid ammonia, although substances such as butadiene and isoprene undergo partial hydrogenation and rearrangement. Here, again, replacement of hydrogen atoms by aryl groups such as the phenyl radical increases reactivity; hydrogen may be displaced or addition to the double bond may take place. Polymerization and/or cleavage of the carbon-carbon double bond may also occur. Styrene is converted in part to ethylbenzene and is also partially polymerized. Stilbene is reduced to 1,2-diphenylethane.

Considerable work has been done with the acetylenic hydrocarbons. Acetylene, itself, is distinctly acidic in liquid ammonia and is converted largely into the monometal derivative. If acetylene (or its derivatives) is allowed to react with a sodium solution in excess, little hydrogen is evolved; considerable reduction to ethylene (or the olefin derivative) takes place. In order to avoid losses by hydrogenation, either sodium amide has been used or the metal and acetylene have been added at such a rate that no excessive quantity of sodium is present. Little reduction of acetylene occurs under such circumstances. The resulting alkali salts may be subjected to alkylation in liquid ammonia for the synthesis of substituted acetylenes, or they may be isolated and treated with alkylating agents in other media.



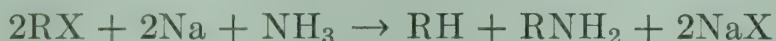
The aromatic hydrocarbons are not attacked by ammonia solutions of metals, at least, in so far as the benzene nucleus is concerned. Naphthalene, however, is reduced by sodium or potassium solutions to

tetrahydronaphthalene with concomitant formation of the alkali amide. It is probable that this reaction



goes through an intermediate organo-alkali compound since the product solutions at low temperatures are always bright red in color. Benzene, toluene, and related compounds can, however, be reduced by the active hydrogen formed as the result of the interaction of metal-ammonia solutions with active hydrogen compounds such as water, alcohols, acid amides, aryl amines, mercaptans, and even aliphatic aldehydes. It should be emphasized again that the benzene nucleus itself is not susceptible to electron reduction, but can be hydrogenated in liquid ammonia by the active hydrogen produced when metal-ammonia solutions react with acidic hydrogen compounds.

HALOGEN COMPOUNDS. One of the most convenient ways for determining halogen in organic compounds makes use of sodium solutions in liquid ammonia to effect rupture of the carbon-halogen bond. The halogen is converted quantitatively into the halide ion. The organic part of the molecule may undergo a variety of reactions. In most instances, however, the fate of the organic portion of the molecule has not been subjected to critical study. Two reactions predominate when a monohalogen substitution product of a paraffin hydrocarbon reacts with metal-ammonia solution. These may be represented by the following equations:



Either the hydrocarbon and the amine may form or an unsaturated hydrocarbon may be obtained. In the latter case, the reaction may represent an example of a dehydrohalogenation by the sodium amide which is usually obtained as one of the products. Methyl chloride gives, very largely, methane; methyl iodide, on the other hand, is converted into methane and methylamine. Normal propyl iodide reacts to form propane, propylamine, together with a small quantity of propene.

Phenyl-substituted alkyl halides may undergo reduction, dimerization, and/or polymerization in so far as the organic portion of the molecule is concerned. Benzylchloride gives toluene, 1,2-diphenylethane, and unidentified solid hydrocarbons.

Unsaturated halides such as acetylene dibromide undergo dehalogenation with the formation of acetylene; the latter may undergo

further reaction with the formation of the metal salt and evolution of hydrogen, which in turn affects some reduction to the olefin. The reactions of bromoolefins in liquid ammonia solutions with sodium have also been investigated, and in all cases both dehydrohalogenation as well as formation of some of the olefin may occur. Paraffin polyhalides likewise undergo dehalogenation and reduction. Symmetrical dichloroethane gives ethylene largely. Unsymmetrical dichloroethane gives ethane with a small amount of ethylene. Chloroform gives methane together with small amounts of acetylene, ethylene, and some cyanide. Methylene chloride gives largely methane. Sodium amide is formed as a by-product in some of these instances.

The reactions of aryl halides are more complicated. When sodium and chlorobenzene react in liquid ammonia, benzene, diphenylamine, and triphenylamine are the principal reaction products, although small quantities of aniline are also obtained. Ortho-dichlorobenzene and sodium react to give benzene and *o*-phenylenediamine.

ALCOHOLS AND PHENOLS. Since ammonia is a basic solvent and accentuates the acid character of hydrogen compounds, it is not surprising to find that alcohols and phenols react with the formation of the corresponding alkali metal derivatives. Primary alcohols are more reactive than the secondary and tertiary alcohols. The sodium alcoholates of secondary and tertiary alcohols are more soluble in liquid ammonia. In some instances, the alcohol reacts only to displace one-half of the potentially acidic hydrogen with the formation of compounds of the type formula $\text{RONa} \cdot \text{ROH}$. Polyhydric alcohols also form salts, but, in these instances, displacement rarely affects more than one of the hydroxyl group. Thus, for instance, ethylene glycol yields only the monoalkali derivative, but does give a completely substituted calcium salt. Unsaturated alcohols may undergo reduction along with formation of the alcoholate as, for example, in accordance with the following equation:



Phenols, being more acidic in character, react somewhat more readily to give the corresponding metal derivatives. In the case of the naphthols, partial reduction occurs. Thus, for instance, naphthols are in part reduced to tetrahydronaphthols.

In so far as carbohydrates are substances which contain hydroxyl groups, it is possible to form metal derivatives by direct reaction with solutions of the alkali and alkaline earth metals in liquid ammonia.

Such sugars as glucose and fructose form the monoalkali salts very rapidly. Extensive work has been done along this line as an approach to the alkylation of carbohydrates. Thus, for instance, starch yields alkali metal derivatives which can be partially, and subsequently completely, methylated. Cellulose may be converted into mono-, di-, or trialkali salts. Such derivatives may be alkylated in liquid ammonia directly or isolated from the ammonia solvent and then be subjected to alkylation in some other medium.

ETHERS. Simple aliphatic ethers do not react with metal-ammonia solutions. It is for this reason that diethyl ether has been used as a solubilizing agent and as an inert diluent where reduction of normally insoluble compounds in liquid ammonia is being effected by sodium or sodium solutions in the presence of ammonium salt. If the ether contains at least one aromatic group, the action of liquid ammonia results in cleavage of the carbon-oxygen bond.

ESTERS. Esters of the simple carboxylic acids undergo both reduction and ammonolysis. Sodium derivatives of alcohols and the acid amides are obtained. Thus, for instance, methyl butyrate gives largely butanol. Ethyl phenylacetate yields phenylethyl alcohol. Methyl cinnamate gives, among other products, β -phenylpropyl alcohol.

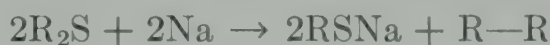


AMINES. Aliphatic amines are generally unreactive towards sodium solutions in liquid ammonia. No salt formation occurs. Aromatic amines, on the other hand, react more readily to give sodium compounds which are to a very large extent solvolyzed. The aromatic amines are also reducible in some instances if the reaction with the metal-ammonia solution is carried out in the presence of an ammonium salt or an alcohol. Thus benzylaniline is reduced to give toluene and aniline as products of such reaction.

AMMONO ACIDS. Acid amides, amidines, related ammono carbonic acids, and ammono acids of the elements exhibit their true character as nitrogen analogs of corresponding aquo derivatives by their behavior in liquid ammonia as a solvent. Acid amides react as monobasic acids to liberate hydrogen and to form the alkali salts. Acid amidines also form monoalkali salts. Urea reacts fairly rapidly with metal-ammonia solutions to form the mono salt and to a limited extent also the dialkali salt. Nitrogen alkylation can be achieved quite readily in all these instances by treatment of the metal derivatives with the alkyl halide directly in liquid ammonia.

Sulfamic acid, a mixed aquo ammono sulfuric acid, $\text{NH}_2\text{SO}_3\text{H}$, behaves as a dibasic acid in liquid ammonia to form the disodium salt. Sulfonamides and presumably also compounds containing the PONH_2 group give alkali metal salts which usually undergo rapid hydrolysis in the presence of water.

SULFUR COMPOUNDS. Sulfur compounds undergo a variety of reactions, depending upon their nature. Mercaptans and thiophenols are rapidly converted into the corresponding sodium salts. The aliphatic sulfides, on the other hand, undergo partial reduction (or what amounts to cleavage of the carbon-sulfur bond) in accordance with the following equations:



An interesting series of syntheses has been accomplished by DuVigneaud and co-workers in the reduction of the disulfide linkage in liquid ammonia. Cystine is reduced by sodium to cysteine. The disodium salt of the latter can be subjected to alkylation to give S-cysteine derivatives. These observations have been extended to the higher homologs of cystine and related amino acids.

NITROGEN COMPOUNDS. Aliphatic nitro compounds act as acids in liquid ammonia. The alkali metal compounds are fairly stable; in the presence of excess metal-ammonia solution some reduction takes place slowly to the corresponding alkyl hydroxylamines. Aromatic nitro compounds, on the other hand, undergo a variety of very interesting reactions, which have been studied only qualitatively. Nitrobenzene can be reduced to the nitroso compound, which in turn is further reducible to the disodium salt of N-phenylhydroxylamine. The latter can be still further reduced to aniline. Nitronaphthalene is reduced by means of sodium in liquid ammonia to give excellent yields of dihydro-1-naphthylamine.

Derivatives of nitramide, NH_2NO_2 (a mixed aquo ammono nitric acid), undergo different reactions, depending upon the nature of the medium. Nitroguanidine is reduced and degraded in part by sodium in liquid ammonia to give cyanamide and nitrogen among the reduction products. If, on the other hand, such reduction is carried out in acid solution, that is, in the presence of an ammonium salt, both nitro- and nitrosoguanidine are converted into aminoguanidine. This is an excellent example of the difference between hydrogen reduction as contrasted with the sort of decomposition and electron reduction that may be effected by solutions of the alkali metals by themselves.

Hydrazine undergoes no extensive reduction or reaction with sodium in liquid ammonia either in the presence or the absence of ammonium salts. However, reduction of substituted hydrazines by means of sodium, or of sodium in the presence of ammonium bromide, takes place in accordance with one of the following general types of reactions:

A. The nitrogen-nitrogen bond in the substituted hydrazine is ruptured by sodium in the presence of ammonium bromide. If two phenyl groups or one phenyl group and some other radical are attached to the same nitrogen atom, rupture of the nitrogen-nitrogen bond can be accomplished by sodium alone.

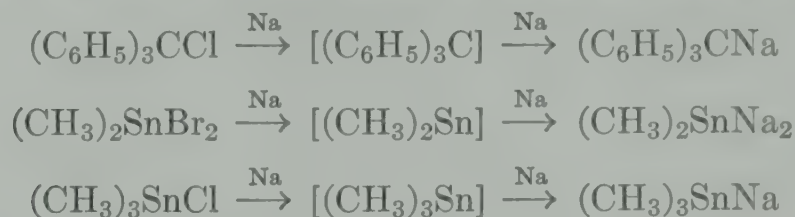
B. Sodium replaces the active hydrogen in substituted hydrazines and the hydrogen thereby liberated serves to reduce the nitrogen-nitrogen bond.

Phenylhydrazine, on treatment with sodium, gives a mixture of sodium phenylhydrazide and sodium anilide. The sodium hydrazine derivatives (better prepared by reaction of the hydrazine with sodium amide in order to prevent reduction) can be alkylated directly in liquid ammonia to form the unsymmetrically disubstituted hydrazines. It is interesting in this connection to point out that azoxybenzene and azobenzene are both reduced to the corresponding disodium salts of hydrazobenzene; the latter can be treated directly in liquid ammonia with an excess of ethyl iodide to give symmetrical diethyl diphenyl hydrazine.

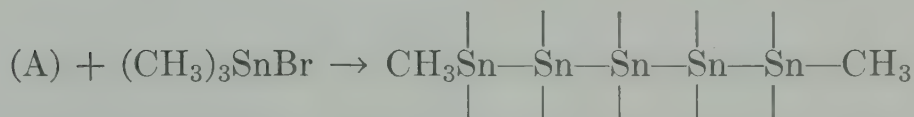
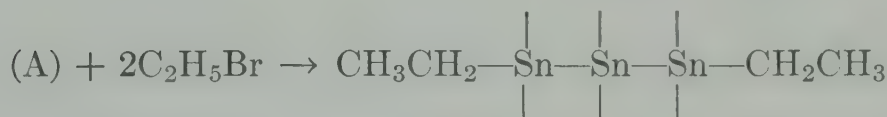
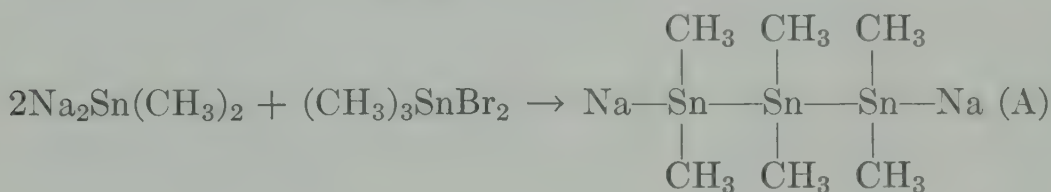
Heterocyclic compounds containing nitrogen often react with the alkali metal solutions in liquid ammonia to form the corresponding salts. Reduction may also occur as is evidenced by the fact that carbazole is reduced (in acid solution) to the tetrahydro derivative. The reduction of 1,2,3-benzotriazole with sodium gives a mixture of the sodium salt of the original compound and the sodium salt of an unstable dihydro derivative. When sodium and ammonium bromide are employed, rupture of the heterocyclic ring system occurs to give *o*-phenylenediamine. Benzimidazole reacts with sodium in ammonia to liberate hydrogen and to form the monosodium salt. If ammonium bromide is present, the unstable dihydro derivative is obtained.

METALLO-ORGANIC COMPOUNDS. Much of the early work on metallo-organic derivatives was accomplished in liquid ammonia and is based upon the experimental observations of Kraus and his co-workers. Such compounds as triphenylmethylchloride, dimethyltindibromide, and trimethyltinchloride are reduced to the corresponding free

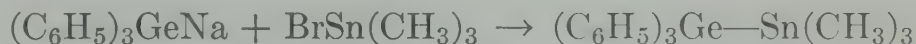
radicals in liquid ammonia. The corresponding sodium derivatives are obtained in the presence of an excess of metal-ammonia solution:



Among the more important results of the investigation of metallo-organic compounds in liquid ammonia is the fact that catenation and formation of mixed chains can be effected directly. Thus, for instance, the synthesis of a variety of alkyl stannanes can be accomplished by the following series of reactions:



A compound containing a germanium-tin linkage, for instance, can be obtained by the following reaction:



In effect, all of these reactions are alkylation procedures which are practically ionic in character when carried out in ammonia as the solvent.

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NITROGEN-CONTAINING SOLVENTS

Many derivatives of ammonia, especially those which exist in the liquid state over a more workable temperature range, have been evaluated as solvents. Many of these possess interesting and unusual properties. It has, therefore, been considered desirable to review briefly the chemical behavior of a selected number of nitrogen-containing solvents. The treatment is not intended to be exhaustive, but illustrative—to show (a) how non-aqueous solvents can be employed to effect interesting and useful chemical reactions and (b) how certain concepts such as those which define the chemical character of solutes in relation to the solvent as a parent substance of a system of compounds make possible the understanding of reactions which take place therein, and (c) to emphasize the importance of acid-base theories generally in their application to non-aqueous systems.

The simple amines and polyamines are discussed first since they are the alcohol and glycol analogs in the nitrogen system of compounds. Pyridine, a cyclic "ammono ether" which has been used widely as a solvent and has been studied by many investigators, is next considered. Hydrazine and hydroxylamine are also discussed, not because they now possess utility as solvents but because of their importance as parent substances of systems of compounds. Since all of these compounds are basic substances, care must be taken in utilizing them as solvents. They tend to absorb both moisture and carbon dioxide rapidly from the atmosphere. Hydrazine and hydroxylamine, furthermore, suffer deterioration through autoxidation (reaction with atmospheric oxygen).

The amazing properties of hydrogen cyanide as a solvent are worthy of mention. Even though its toxicity is a serious deterrent, it has been studied quite thoroughly with recorded experimental observations constituting valuable information which has contributed to an extension of knowledge of non-aqueous systems. Acetonitrile has also been used as a solvent. Related to hydrogen cyanide and acetonitrile are the simple amides, formamide and acetamide, respectively, both

of which certainly deserve more thorough study as non-aqueous solvents.

As new nitrogen compounds are synthesized and/or made available as chemical commodities, consideration of such materials as solvents for both inorganic and organic substances merits attention. Mention is made specifically of the polyethylene amines and their N-substitution products, of the alkylol amines, the morpholines, and of aliphatic nitro compounds. The opportunities offered by use of these solvents in all branches of chemistry, both theoretical and applied, have been explored or exploited to only a limited extent.

ALIPHATIC AMINES

THE SIMPLE AMINES. Relatively little work has been carried out on the solvent characteristics of the aliphatic derivatives of ammonia. The simple amines have been investigated only in a qualitative fashion as solvents and ionizing media for inorganic substances. Only one polyamine, namely, ethylenediamine, has been studied to any degree. It is worthy of more extensive investigation particularly as a medium for chemical reactions.

The mono-substituted amines, as a class, possess very low viscosities, being much more mobile than water. However, salt solutions are generally of high viscosity; the more concentrated solutions frequently approach the consistency of thick molasses (1).

The solvent power of the amines for ionic compounds is definitely inferior to that of the parent substance, liquid ammonia. Moreover, the ability to dissolve inorganic substances usually decreases markedly with increasing length of the hydrocarbon chain. Thus, for example, potassium iodide is very soluble in liquid ammonia, possesses a moderate solubility in methylamine, but displays only a very limited solubility in ethylamine (2). A similar effect is frequently noted in passing from primary to secondary to tertiary amines (1, 3).

Although methylamine is greatly inferior to liquid ammonia in its solvent power, it is nevertheless a fair solvent for inorganic substances as shown by the qualitative data presented in Table 23 (1).

The simpler primary amines possess to a limited extent the ability to dissolve alkali metals to yield blue solutions (4, 5, 6). Lithium and cesium are soluble in methylamine, whereas sodium and potassium are insoluble. The solubility of lithium decreases with increasing hydrocarbon chain length of the amine; although the element possesses some degree of solubility in ethylamine, it is insoluble in *n*-propyl-

TABLE 23

SOLUBILITY OF INORGANIC SUBSTANCES IN METHYLAMINE

(Room temperature; A indicates solvate formation)

	<i>Very Soluble</i>	<i>Moderately Soluble</i>	<i>Slightly Soluble</i>	<i>Insoluble</i>
S	Sr(NO ₃) ₂	P ₄ (white)	P ₄ (red)	CuSO ₄
Br ₂	Ba(SCN) ₂	NaClO ₃	Na ₂ SeO ₄	Ag ₂ SO ₄ (A)
I ₂	BaI ₂ (A)	Ca(NO ₃) ₂	KNO ₃	CaC ₂
LiCl	Hg(CN) ₂	BiCl ₃ (A)	K ₂ PtCl ₆	ZnS
NaNO ₃	HgI ₂		CuHAsO ₃	SnI ₄ (A)
KSCN	TiNO ₃		CuS	Cr ₂ (SO ₄) ₃
CuSCN	Pb(SCN) ₂ (A)		Ag ₂ SO ₃	Fe ₂ (SO ₄) ₃ (A)
AgNO ₃	BiI ₃ (A)		Ba(NO ₃) ₂	NiSO ₄
AgI			Hg(SCN) ₂	
			PbI ₂ (A)	
			Bi ₂ S ₃	
			UO ₂ (C ₂ H ₃ O ₂) ₂	

amine. Secondary and tertiary amines are incapable of dissolving lithium, sodium, or potassium.

The behavior of amines as ionizing media parallels their solvent powers. Thus solutions in liquid ethylamine show conductivities which lie between those in methyl and normal amylamines (2); diethylamine is a distinctly poorer ionizing solvent than the corresponding primary amine (3). Tertiary amines apparently possess little or no ability to act as electrolytic media. The conductivity curves for electrolytes in amines are generally typical of those obtained in solvents of low dielectric constant, the molecular conductance first rising to a maximum with increasing dilution, then falling to a minimum, and finally increasing again toward a final maximum (3, 7).

No systematic attempt has been made to study the simple amines as parent solvents of systems of acids, bases, and salts. One investigation has demonstrated that the solvolysis of ethylphenylacetate in *n*-butylamine* is catalyzed by substances capable of acting as acids in this medium (8).

The solvolytic reaction:



* Many weakly acidic compounds can be titrated in butylamine as a solvent, using a standard solution of sodium methoxide in benzene-methanol with thymol blue as indicator (Fritz and Lisicki, *Anal. Chem.*, **23**, 589 [1951]).

which ordinarily proceeds very slowly, is markedly accelerated by the addition of *n*-butylammonium salts. Since such onium salts yield the cation characteristic of the solvated proton in butylamine, they have been regarded as constituting acidic solutions. The magnitude of the catalytic effect is dependent upon the nature of the butylammonium salt present, the specific anion order being the following:



This order is very similar to that noted for the catalytic effect exerted by ammonium salts on the ammonolysis of esters in liquid ammonia (9, 10).

ETHYLENEDIAMINE. Largely because of its ready availability and its similarity to water in physical properties, ethylenediamine has been the most extensively investigated of the polyamines. The pure anhydrous liquid may be prepared from the commercially available hydrate (60 to 70%) or the 95% product in the following fashion (11): The commercial material is allowed to stand over a mixture of sodium hydroxide and barium oxide for several days and is then further dehydrated by storage for one day over metallic sodium. The ethylenediamine is then fractionally distilled from freshly activated alumina into a receiver containing a mixture of alumina and sodium hydroxide. Some important physical properties of the pure liquid are given in Table 24.

TABLE 24

SOME PHYSICAL CONSTANTS OF ETHYLENEDIAMINE

<i>Property</i>	<i>Value</i>
Freezing point, °C.	11.0 (12)
Boiling point, °C.	116.2 (12)
Density, grams per cc. at 25°C.	0.891 (11)
Viscosity, centipoise, at 25°C.	1.725 (12)
Dielectric constant, at 25°C.	12.9 (11)
Heat of vaporization, kcal. per mole at 20°C.	11.2 (12)
Specific conductivity, ohm ⁻¹	9×10^{-8} (11)

The liquid range of ethylenediamine is a convenient one for experimentation. The chief difficulty encountered in its use is that, because of its highly basic character, it absorbs water and carbon dioxide rapidly. Its dielectric constant compares favorably with that of most non-aqueous solvents. The relatively high value for the heat of vaporization indicates considerable association in the liquid state and consequent polar nature.

The solubilities of a number of inorganic salts in ethylenediamine have been determined quantitatively (13). The comparative solubility behavior of these substances in ethylenediamine, liquid ammonia, and water is presented in Table 25.

TABLE 25
COMPARATIVE SOLUBILITIES OF SOME SALTS AT 25°C.
(All data in grams of salt per 100 g. of solvent.)

<i>Salt</i>	<i>Ethylenediamine</i>	<i>Ammonia</i>	<i>Water</i>
NaCl	0.33	3.02	35.98
NaBr	54.4	138.0	94.6
NaI	34.6	161.9	183.7
NaCNS	93.5	205.5	142.6
NaNO ₃	33.5	97.60	91.5
NaClO ₃	52.8	106
NaClO ₄	30.1	209.6
NaIO ₃	0.00	9.4
KCl	0.014	0.04	35.85
KBr	0.78	13.50	68.3
KI	74.9	182.0	148.7
KCNS	83.0	239
KNO ₃	0.37	10.4	37.9
KClO ₃	0.145	2.52	8.6
KClO ₄	2.81	2.07
KBrO ₃	0.00	0.002	8.0
KIO ₃	0.00	0.000	10.6
KIO ₄	Reaction	0.51
LiCl	1.39	1.41 (0°)	84.66
LiBr	2.41	170
CaCl ₂	0.00	83
SrCl ₂	0.00	55.8
BaCl ₂	0.22	0.00	37.2
HgCl ₂	0.4	7.2
Hg(C ₂ H ₃ O ₂) ₂	0.186	25.(10°)

It is evident, from the data available, that ethylenediamine, although not so good a solvent as liquid ammonia, is qualitatively similar in its solvent behavior. The chlorides are usually only sparingly soluble in either solvent. Moreover, the relatively high solubility of sodium bromide and iodide, and potassium iodide, in comparison with the chlorides, differentiates both ethylenediamine and liquid ammonia from water. Although several salts are more soluble in liquid ammonia than in water, potassium perchlorate is the only salt tested which possesses a greater solubility in ethylenediamine than in water. Ethylenediamine forms solvates with essentially the same salts with

which water forms stable hydrates, for example, $\text{NaI} \cdot 2\text{H}_2\text{O}$, $\text{NaI} \cdot 3\text{en}$; $\text{NaClO}_4 \cdot \text{H}_2\text{O}$, $\text{NaClO}_4 \cdot 3\text{en}$; $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{SrCl}_2 \cdot 6\text{en}$. Reference should be made in this connection to the bidentate character of ethylenediamine. Such solvates are, therefore, considerably more stable than those formed by the simpler primary amines.

The electrical conductivities of a few salts in ethylenediamine have been determined. Representative conductivity data are shown in Table 26.

TABLE 26

CONDUCTIVITIES OF SOME SALTS IN ETHYLENEDIAMINE AT 25°C.

<i>Salt</i>	<i>Concentration</i>	Λ , <i>ohms</i> ⁻¹	Λ_∞ , <i>ohms</i> ⁻¹
KI	2.334 (12)	16.0	
	0.279 (12)	16.0	
	0.004595 (11)	27.8	
	0.000049 (11)	65.5	69.2 (11)
NaClO_4 (12)	2.212	12.6	
	0.290	17.4	
NaBr (12)	2.305	8.77	
	0.218	10.8	
NaI (12)	1.259	14.2	
	0.328	16.4	
AgNO_3 (11)	0.003340	29.7	61.4
	0.000087	56.0	
AgI (11)	0.006615	4.79	48.8
	0.000140	21.95	

The values for the conductivities indicate a fairly high degree of dissociation for all the salts examined, except silver iodide. The relatively low conductance value for this substance is attributed to the partial covalent character of the silver-iodine bond.

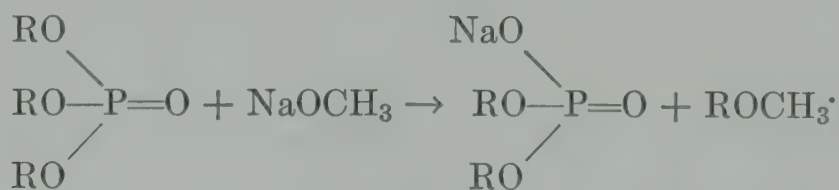
Solutions of sulfur in ethylenediamine are excellent conductors (12). The solutions are rather unstable at room temperature; brisk evolution of ammonia occurs at 60°C. That the final product of reaction between sulfur and ethylenediamine is not responsible for the conductivity of the solutions is demonstrated by the fact that the conductivity decreases slowly with time at 25°C., at which temperature slow evolution of ammonia also takes place.

Attempts to electrodeposit some of the more active metals from ethylenediamine solutions have yielded the following interesting results (12). The electrolysis of a 20% solution of anhydrous magnesium perchlorate between a copper cathode and a magnesium anode results in the deposition of the metal as a black powder. Lithium is presumably plated out as a brown powder from a bromide solution in

a cell having a lithium amalgam anode and a copper cathode. At 100°C., pure sodium is deposited at current efficiencies greater than 90% from an electrolyte containing 25% potassium iodide and 5% sodium iodide, the electrodes consisting of a 0.5% sodium amalgam anode and a copper cathode. With potassium iodide as electrolyte and the metal amalgam as anode, potassium is also liberated at 100°C. with high current efficiencies.

Anhydrous ethylenediamine has proved a useful medium for carrying out certain analytical determinations (14). Thus organic chlorides (for example, chloroform, carbon tetrachloride, ethylene dichloride, butyl chloride, dichloroethyl ether) react at 100°C. with an excess of ethylenediamine to form secondary amines and amine hydrochlorides. The latter have the character of "strong" acids in anhydrous ethylenediamine and are titrated with standard sodium hydroxide in a methanol-ethylenediamine solution, "azo-red" (2,4-dihydroxyazobenzene-4-sulfonate) serving as the indicator. An alternative method employs an excess of standard sodium hydroxide solution—ethylenediamine mixture as the reactant. In this case, substituted amines and sodium chloride are produced, and the unconsumed sodium hydroxide is titrated with standard acetic acid in pyridine, thymolphthalein acting as indicator. Esters interfere in the determination of organic chlorides. Compounds which undergo acidic or alkaline dissociation in anhydrous ethylenediamine must be determined independently so that suitable corrections can be made for their presence.

An interesting determination is that of Flexol plasticizer TOF (tri-[2-ethylhexyl] phosphate). The plasticizer is treated with an excess of sodium methoxide in anhydrous ethylenediamine, the following reaction probably occurring:



The unreacted sodium methoxide is titrated with standard ammonium chloride in methanol-ethylenediamine solution in the presence of "azo-red" indicator. The success of the titration is dependent on the fact that the acid character of ammonium chloride, which is a weak acid in water, is considerably enhanced by the basic nature of ethylenediamine. Esters, organic halides, pyrophosphates, and acids interfere in the analysis; they must be determined independently and a suitable correction applied.

PYRIDINE

The organic chemist has long used pyridine as a reactant and reaction medium; the inorganic chemist, however, has been interested mainly in the ability of this compound to act as a coordinating agent in the formation of a wide variety of complex compounds. Publications dealing with anhydrous pyridine and covering solubility relationships, reactions of inorganic substances, and the electrochemical behavior of inorganic and organic solutes, although few in number, are revealing. It is with these aspects of pyridine chemistry that the survey which follows is primarily concerned. No attempt is made to discuss the great multiplicity of complex compounds containing pyridine.

PREPARATION AND PHYSICAL PROPERTIES. Commercially available pyridine contains varying quantities of moisture and related organic homologs; dehydration and fractionation are required to obtain a material which is suitable for research purposes. Purification may be accomplished by permitting the commercial product to stand over potassium hydroxide or barium oxide for approximately one week and then subjecting the dehydrated material to fractional distillation. Active alumina has also been employed to remove traces of moisture. The properties of pyridine are given in Table 27.

TABLE 27

SOME PHYSICAL CONSTANTS OF PYRIDINE

<i>Property</i>	<i>Value</i>
Freezing point, °C.	-40.7
Boiling point, °C.	115.5 (760 mm.)
Specific conductivity, ohm ⁻¹	5.3×10^{-8} (18°C.) *
Density, grams per cc.	1.00304 (0°/4°C.)
Dielectric constant	12.5 (20°C.)
Viscosity, centipoise	0.945 (20°C.)

* Values of less than 1×10^{-9} for the specific conductance have been obtained with very carefully purified pyridine (20).

SOLUBILITIES IN ANHYDROUS PYRIDINE. Even though pyridine has a relatively low dielectric constant and should therefore be a poor solvent for ionic compounds, it is surprising that many inorganic salts possess appreciable solubility in this medium; this may be attributed in large measure to the high solvating power of pyridine. A fairly complete listing of recorded qualitative solubilities follows (15, 16, 17):

Soluble Salts. LiCl, LiBr, LiI, LiNO₃, NaBr, NaI, NaSCN, NaNO₂, KCN, KSCN, KMnO₄, NH₄SCN, CuCl, CuBr, CuSCN, CuF₂, AgSCN,

AgNO₂, AgNO₃, AgC₂H₃O₂, Ag₂SO₄, AuCl₃, BeCl₂, MgCl₂, MgBr₂, MgI₂, CaCl₂, CaBr₂, CaI₂, Ca(NO₃)₂, SrCl₂, SrI₂, BaCl₂, BaI₂, ZnCl₂, ZnBr₂, Zn(CN)₂, Zn(SCN)₂, CdI₂, Cd(SCN)₂, HgCl₂, HgBr₂, HgI₂, Hg(CN)₂, K₂HgI₄, AlBr₃, SnCl₂, SnBr₂, SnCl₄, Pb(SCN)₂, PbCl₂, Pb(NO₃)₂, Pb(C₂H₃O₂)₂, TiF₄, CrCl₂, CrO₃, MnCl₂, PtCl₄, LaCl₃, CeCl₃, CeBr₃, UBr₄, UO₂Cl₂, UO₂I₂, UO₂(NO₃)₂, FeCl₂, and FeCl₃.

Difficultly Soluble or Insoluble Salts. LiOH, NaCl, KOH, KNO₃, KCl, KBr, KI, NH₄Cl, NH₄I, CuCN, Cu(NO₃)₂, BaBr₂, Ba(NO₃)₂, CdCl₂, CdBr₂, Cd(NO₃)₂, Hg(NO₃)₂, AlCl₃, PbBr₂, PbI₂, SbCl₃, BiCl₃, CrCl₃, Co(NO₃)₂, and Ni(NO₃)₂. In addition to the specified salts, the following are insoluble: the salts of rubidium, cesium, and mercury(I); the chlorates, perchlorates, bromates, and iodates of lithium, sodium, and potassium; the borates, carbonates, silicates, phosphates, arsenites, arsenates, sulfides, sulfites, and chromates of uni- and multivalent ions.

A few generalizations regarding solubilities may be made. Chlorides, bromides, iodides, thiocyanates, and acetates are usually soluble. The general order of solubility in the halogen family decreases from the iodides to the chlorides. Compounds containing oxy anions, with the frequent exception of nitrates, are insoluble. Most metal fluorides possess very slight solubility.

ELECTROCHEMICAL STUDIES IN PYRIDINE. The most extensive studies of the conductance of inorganic and organic salts in anhydrous pyridine have been those of Walden, Audrieth and Birr (18) and of Kraus and collaborators (19, 20). The former investigators, in measurements up to dilutions of 50,000 liters per mole, observed marked differences in the strengths of various solutes, the orders of diminishing conductance being $\text{Ag}^+ > \text{Li}^+ > \text{K}^+ > \text{Na}^+$ and $\text{Pi}^- * > \text{ClO}_4^- > \text{I}^- > \text{NO}_3^- > \text{Br}^- > \text{Cl}^-$. Kohlrausch's square-root law was found to be applicable to strong and moderately strong electrolytes at dilutions exceeding approximately 8000 liters per mole, and the validity of the principle of independent ion migration was established for several of the salts.

Conductivity values obtained by Kraus and co-workers are summarized in Table 28. The method of Fowler and Kraus (21) was employed to evaluate ion conductances at infinite dilution, and that of Fuoss (22) was used to find the limiting equivalent conductances and dissociation constants of the salts investigated.

Conductivity studies by Hantzsch and Caldwell (23) have demonstrated that pyridine acts as a differentiating solvent toward "strong"

* Pi⁻ signifies the picrate ion.

TABLE 28

CONDUCTANCE OF SALTS IN PYRIDINE AT 25°C.

<i>Salt</i>	Λ_0	Λ_0^+	Λ_0^-	$K \times 10^4$
$(C_4H_9)_4N\text{Pi}$	57.7	24.0	33.7	12.8
$(C_4H_9)_4N\text{Br}$	75.3	51.3	2.5
$(C_4H_9)_4NI$	73.1	49.1	4.1
$(C_4H_9)_4NNO_3$	76.6	52.6	3.7
$(C_4H_9)_4NC_2H_3O_2$	76	52	1.7
$(C_4H_9)_4NFB(C_6H_5)_3$	48.0	24.0	13.2
$(CH_3)_4N\text{Pi}$	76.7	43.0	33.7	6.7
$C_2H_5(CH_3)_3N\text{Pi}$	75.5	41.8	8.2
$(HOC_2H_4)(CH_3)_3N\text{Pi}$	67.0	33.3	1.5
$(BrC_2H_4)(CH_3)_3N\text{Pi}$	67.1	33.4	5.8
$(BrCH_2)(CH_3)_3N\text{Pi}$	71.5	37.8	4.8
$C_5H_5N(C_6H_5)\text{Pi}$	66.3	32.6	11.5
$(C_6H_5)(CH_3)_2(OH)N\text{Pi}$	62.3	28.6	12.3
$C_5H_5NHNO_3$	102.2	49.6	52.6	0.51
$C_5H_{10}NH_2NO_3$	91.1	38.5	0.18
$(C_2H_5)(C_6H_5)_3As\text{Pi}$	57.7	24.0	33.7	19.4
$AgNO_3$	86.9	34.3	52.6	9.3
$AgClO_4$	81.9	47.6	19.1
$Ag\text{Pi}$	68.0	33.7	30.6
$Li\text{Pi}$	58.6	24.9	0.83
$Na\text{Pi}$	60.5	26.8	0.43
$K\text{Pi}$	65.7	32.0	1.0
$NH_4\text{Pi}$	80.5	46.8	2.8
NaI	75.2	26.8	48.4	3.7
KI	80.4	32.0	2.1
NH_4I	95.2	46.8	2.4

acids. The following order of relative strength, as determined by conductance measurements (Table 29), is obtained: $HI > HNO_3 >$

TABLE 29

EQUIVALENT CONDUCTANCES OF SOME ACIDS IN PYRIDINE AT 25°C.

<i>Acid</i>	<i>Concentration</i>	
	<i>N/32</i>	<i>N/64</i>
HI	27.4	31.2
HNO_3	8.38	10.2
HBr	7.12	8.42
HCl	1.16	1.42
C_6H_5COOH	0.022	0.028

$HBr > HCl$.* Organic acids are exceedingly poor conductors in pyridine.

* It is to be understood that in pyridine these substances form pyridinium salts of the formula $C_5H_5NH^+, X^-$.

It should be emphasized that even the so-called strong acids are relatively poor conductors in this medium of low dielectric constant. Of the various inorganic acids which have been investigated in pyridine, perchloric acid has proved to be the most highly ionized. The following dissociation constants having been reported (24): HClO_4 , 7.55×10^{-4} ; HNO_3 , 4.96×10^{-5} ; HI , 5.9×10^{-6} .

Several investigations have been reported dealing with potential measurements in pyridine. The potentials of pure aluminum and of a 2% aluminum amalgam in a saturated solution of aluminum bromide in pyridine have been determined at 25°C. against the electrode, $\text{Ag}/\text{AgNO}_3(0.1 \text{ N})$ in pyridine (25). The values of the electrode potentials referred to the normal calomel electrode* were found to be 0.827 volt for pure aluminum and 1.6 volts for the 2% amalgam at 25°C.

Partington and Skeen (27) have studied the oxidation-reduction potentials of the systems Pt/CuCl , CuCl_2 and Pt/FeCl_2 , FeCl_3 in anhydrous pyridine, using copper and silver in pyridine solutions of their chlorides as reference electrodes. The potential of the electrode apparently arises without the intervention of the solvent, the electrode metal alone taking part in the transfer of electrons between the ions of different oxidation state.

The use of pyridine as a medium for the electrodeposition of metals has received attention, particularly by Müller and his co-workers. These investigators took special pains to ensure the use of absolutely anhydrous solvent and solutes and thus succeeded in discharging metals from solutions of their salts in pyridine where previous investigators had failed. Decomposition potentials of various metallic ions, as well as single potentials of the metals containing the respective ions in pyridine, were determined. A summary of successful experimental efforts to electrodeposit metals from pyridine solutions is given in Table 30.

Attempts to obtain the respective metals by electrolysis of solutions of aluminum chloride, cerium(III) chloride, manganese(II) chloride, beryllium bromide, uranyl chloride, and radium bromide proved unsuccessful.

In a study concerned primarily with a search for suitable reference electrodes for use in anhydrous pyridine, the following decomposition potentials were reported for saturated solutions at 30°C.: zinc chloride, 1.75 volts; cadmium chloride, 1 volt; mercury(II) chloride, 0.65 volt;

* The calomel electrode in water has approximately the same potential as $\text{Ag}/\text{AgNO}_3(0.1 \text{ N})$ in pyridine (26).

TABLE 30

ELECTRODEPOSITION OF METALS FROM PYRIDINE SOLUTIONS (28)

<i>Metal</i>	<i>Solute</i>	<i>Metal Base</i>
Li	LiCl, LiNO ₃	Pt or Fe
Na	NaI, NaNO ₃ , NaSCN	Pt, Hg
K	KSCN	Pt, Hg
Ca	Ca(NO ₃) ₂	Pt
Ba	BaI ₂	Hg
Ag	AgNO ₃	Pt
Cu	CuI	Pt
Fe	FeCl ₂	Pt
Pb	Pb(NO ₃) ₂	Pt
Mg	MgBr ₂	Pt
Zn	ZnI ₂	Pt

copper(I) chloride, ca. 0.5 volt; and copper(II) chloride, 0.7 volt. The Cd-Hg/CdCl₂ and Zn-Hg/ZnCl₂ reference electrodes were found to be the most satisfactory of all the electrodes tested (29).

A few interesting observations have been made regarding the electrolysis of elementary bromine and some iodine compounds in anhydrous pyridine. In the electrolysis of bromine-pyridine solutions, bromine is transferred from the anolyte to the catholyte at the rate of 2 moles per Faraday of electricity (30). It is proposed that bromine dissociates in pyridine in accordance with the equation:



Electrolysis of compounds of the type RCONHX (X = Cl, Br, or I) results in the deposition of halogen at the cathode (31). Upon electrolysis of cyanogen iodide in pyridine, iodine is produced at the cathode; in other solvents (for example, benzene, acetonitrile, nitrobenzene, aniline), the halogen is deposited at the anode (32). The hypothesis has been advanced that cyanogen iodide behaves as an electromer capable of dissociating in accordance with the following equilibria, depending upon the nature of the solvent:



REACTIONS IN ANHYDROUS PYRIDINE. Few elementary substances are soluble in pyridine. For most of those which do dissolve, there is evidence that they enter into reaction with the solvent. Sulfur has been reported to be soluble in pyridine (15). The halogens possess great solubility; addition of water to an iodine-pyridine solution results in the precipitation of an unstable monosolvate, C₅H₅N·I₂ (33).

The behavior of the alkali metals toward pyridine is particularly interesting (34, 35, 36). Lithium and sodium react very rapidly with pyridine, whereas potassium, rubidium, or cesium react exceedingly slowly. When sodium is treated with an excess of pyridine in a nitrogen atmosphere, the red solution which is first formed turns an opaque deep-green, and a dark green substance of the formula $\text{Na} \cdot 2\text{C}_5\text{H}_5\text{N}$ separates. This disolvate is converted to the brown monosolvate when heated for 2 to 3 hours at 130°C . and at a pressure of 15 mm. of mercury. The last molecule of pyridine cannot be removed, carbonization resulting at 250 to 300°C . Both the di- and monosolvate ignite spontaneously in air. Cautious atmospheric oxidation causes most of the sodium to be converted to the peroxide. Lithium also forms the two solvates, both of which carbonize in air without igniting.

A few metathetical and oxidation-reduction reactions involving simple inorganic compounds in pyridine have been described (15, 16). They are summarized in Table 31. Additional information is given by Walden (37).

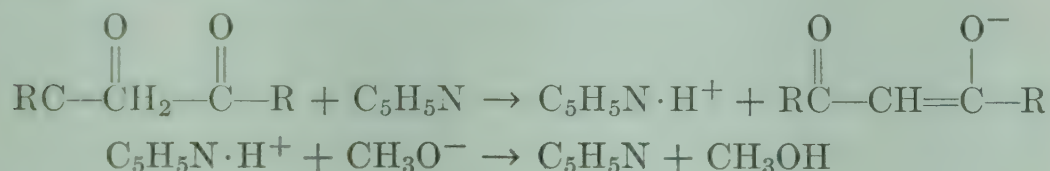
TABLE 31

REACTIONS BETWEEN INORGANIC SUBSTANCES IN PYRIDINE

<i>Reactants</i>	<i>Observation</i>
$\text{CuCl}_2 + \text{H}_2\text{S}$	CuS precipitated
$\text{CuCl}_2 + \text{Ag}_2\text{SO}_4$	CuSO_4 precipitated slowly
$\text{CuCl}_2 + \text{Pb}(\text{NO}_3)_2$ or AgNO_3	$\text{Cu}(\text{NO}_3)_2$ precipitated slowly
$\text{CuCl}_2 + \text{MSCN}$	$\text{Cu}(\text{SCN})_2 + \text{MCl}$ formed (general reaction)
$\text{CuCl}_2 + \text{MBr}_x$	CuBr_2 formed in solution
$\text{CuCl}_2 + \text{NH}_4\text{I}$	NH_4Cl precipitated
$\text{AgNO}_3 + \text{H}_2\text{S}$	Ag_2S precipitated
$\text{AgNO}_3 + \text{KSCN}$	KNO_3 precipitated
$\text{AgNO}_3 + \text{SrCl}_2$	$\text{Sr}(\text{NO}_3)_2$ precipitated
$\text{AgNO}_3 + \text{BaI}_2$	$\text{Ba}(\text{NO}_3)_2$ precipitated
$\text{AgNO}_3 + \text{K}_2\text{HgI}_4$	KNO_3 precipitated
$\text{Ag}_2\text{SO}_4 + \text{MX}_y$	metal sulfates precipitated
$\text{HgX}_2 + \text{H}_2\text{S}$	HgS precipitated
$\text{HgCl}_2 + \text{NH}_4\text{SCN}$	NH_4Cl precipitated
$\text{HgCl}_2 + \text{SnCl}_2$	Hg precipitated
$\text{Hg}_2\text{SO}_4 + \text{I}_2$	HgSO_4 and HgI_2 formed
$\text{FeCl}_3 + \text{CuCl}$	FeCl_2 and CuCl_2 formed
$\text{FeCl}_3 + \text{SnCl}_2$	FeCl_2 and SnCl_4 formed
$\text{FeCl}_2 + \text{X}_2(\text{Cl}_2, \text{Br}_2, \text{or } \text{I}_2)$	Ferric ion formed

ANALYTICAL DETERMINATIONS IN PYRIDINE. The fact that in pyridine the acidic character of weak acids is enhanced has led to some interesting analytical uses of this solvent (14). Thus, as a result of the rapid enolization of β -dicarbonyl compounds (for example, ethyl-

acetoacetate, acetoacetanilide, benzoylacetone, dibenzoylmethane) in this medium, it is possible to determine these substances by titration with a standard solution of sodium methoxide:



A 1% solution of thymolphthalein in pyridine serves as a suitable indicator. Compounds, such as organic acids and their anhydrides, which are acidic to the indicator in pyridine also react with the methoxide and interfere with the determination.

Another determination which has been carried out in pyridine is that of sodium hydroxide in the presence of amines. Amines and other weak bases are neutral to thymolphthalein indicator, whereas sodium hydroxide is strongly basic and may be titrated with a standard solution of acetic acid in pyridine. In the presence of large amounts of sodium chloride, it is necessary to treat the sample with an excess of the standard acetic acid solution and back-titrate with sodium methoxide.

HYDRAZINE

Interest in the use of hydrazine as a specialty fuel and the prospect of its production on a rather substantial scale warrant specific attention to this substance as a solvent and as the parent substance of a system of compounds. Hydrazine resembles ammonia and water in many respects. It is also related generically to hydrogen peroxide and hydroxylamine. The physical properties of hydrazine are given in Table 32.

TABLE 32

PROPERTIES OF HYDRAZINE

Melting point, °C.	2°
Boiling point, °C.	113.5° (1 atm.)
Density, grams/cc.	1.014 (15°C.)
Heat of fusion, kcal./mole	3.2
Heat of vaporization, kcal./mole	10.7 (25°C.)
Dielectric constant	51.7 (25°C.)
Heat of combustion, kcal./mole	148.6

It will be noted that hydrazine possesses a rather convenient liquid range, that it has a high heat of vaporization and is, therefore, a highly associated substance, and that it has a high dielectric constant which

TABLE 33

SOLUBILITIES IN ANHYDROUS HYDRAZINE

(Grams/cc. N_2H_4 at room temperature)

<i>Compound *</i>	<i>Solubility</i>	<i>Compound *</i>	<i>Solubility</i>
AlCl_3	s.s.	$\text{Pb}(\text{NO}_3)_2 \uparrow$	0.52
$\text{AlI}_3 \uparrow$	Pb_3O_4	s.s.
$\text{NH}_4\text{Br} \uparrow$	1.10	Li_2CO_3	ins.
$\text{NH}_4\text{Cl} \uparrow$	0.75	LiCl	0.16
$\text{NH}_4\text{NO}_3 \uparrow$	0.78	MgCO_3	ins.
$(\text{NH}_4)_2\text{C}_2\text{O}_4 \uparrow$	0.44	MgCl_2	s.s.
$(\text{NH}_4)_3\text{PO}_4$	ins.	Mg_3N_2	ins.
$\text{NH}_4\text{VO}_3 \uparrow$	s.s.	$\text{Mg}_3(\text{PO}_4)_2$	ins.
$\text{Sb}_2\text{O}_3 \uparrow$	s.s.	MgSO_4	ins.
SbOCl	s.s.	MnCl_2	0.13
$\text{Sb}_2\text{S}_5 \uparrow$	ins.	MnSO_4	s.s.
$\text{H}_3\text{AsO}_3 \S$	s.s.	$\text{HgC}_2\text{H}_3\text{O}_2 \S$	s.s.
BaCl_2	0.31	$\text{Hg}_2\text{Cl}_2 \S$	s.s.
$\text{Ba}(\text{NO}_3)_2$	s.s.	$\text{HgNO}_3 \S$	s.s.
BaO	ins.	$\text{HgCl}_2 \S$	s.s.
BaSO_4	ins.	$\text{HgI}_2 \S$	0.69
$\text{BiCl}_3 \S$	s.s.	$\text{HgO} \S$
H_3BO_3	0.55	HgS
BN	ins.	$\text{NiCl}_2 \uparrow$	0.08
CdBr_2	0.40	$\text{Ni}(\text{NO}_3)_2 \uparrow$	s.s.
CdCO_3	ins.	$\text{NiSO}_4 \uparrow$	ins.
CdI_2	0.84	$\text{K}_2\text{Cr}_2\text{O}_7$	s.s.
CdS	ins.	KBr	0.60
$\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$	s.s.	KCl	0.09
CaCl_2	0.16	K_2CO_3	s.s.
CaO	ins.	K_2CrO_4	s.s.
$\text{CeCl}_3 \uparrow$	s.s.	KIO_3	s.s.
$\text{Ce}(\text{NO}_3)_3 \cdot \text{NH}_4\text{NO}_3? \uparrow$	ins.	KI	1.75
$\text{Ce}_2(\text{SO}_4)_3$	ins.	$\text{K}_3\text{Fe}(\text{CN})_6 \uparrow$	s.s.
$\text{CrCl}_3 \uparrow$	0.13	KNO_3	0.14
Cr_2O_3	ins.	$\text{KMnO}_4 \uparrow$	s.s.
$\text{CrO}_3 \uparrow$	s.s.	K_2SO_4	0.05
$\text{Co}(\text{C}_2\text{H}_3\text{O}_2)_2 \uparrow$	s.s.	$\text{AgCl} \S$	ins.
$\text{CoCl}_2 \S$	s.s.	$\text{AgNO}_3 \S$	s.s.
$\text{CuCl}_2 \uparrow$	0.05	$\text{NaC}_2\text{H}_3\text{O}_2$	0.06
$\text{Cu}(\text{NO}_3)_2 \S$	s.s.	$\text{NaBrO}_3 \uparrow$	s.s.
$\text{CuSO}_4 \S$	s.s.	NaBr	0.37
CuS	ins.	Na_2CO_3	ins.
$\text{FeSO}_4 \uparrow$	s.s.	NaClO_3	0.66
$\text{FeS} \uparrow$	0.09	NaCl	0.08
$\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \S$	ins.	NaNO_3	1.00
$\text{PbF}_2 \S$	0.06	NaI	0.64
$\text{Pb}(\text{BO}_2)_2$	s.s.	Na_2SO_4	ins.
$\text{PbCl}_2 \S$	s.s.	SrCl_2	0.08
$\text{PbI}_2 \S$	s.s.	$\text{Sr}(\text{NO}_3)_2$	s.s.

TABLE 33 (*Continued*)
 SOLUBILITIES IN ANHYDROUS HYDRAZINE
 (Grams/cc. N_2H_4 at room temperature)

<i>Compound *</i>	<i>Solubility</i>	<i>Compound *</i>	<i>Solubility</i>
SrSO_4	ins.	NdCl_3	ins.
$\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2$	s.s.	PdCl_2 §	s.s.
ZnCO_3	ins.	PtCl_4 §	s.s.
ZnCl_2	0.08	PrCl_3	ins.
ZnSO_4	ins.	$\text{Sm}_2(\text{SO}_4)_3$	s.s.
$\text{Zn}_3(\text{PO}_4)_2$	ins.	RbCl	s.s.
ZnS	ins.	S †	0.54
LaCl_3	ins.		

ins., insoluble.

s.s., slightly soluble; less than 0.05 g./cc. N_2H_4 .

* No indication is given in the original article concerning exact composition of compound listed. They have been assumed to be anhydrous.

† Visible reaction.

‡ Solvolysis.

§ Probable reduction to metal.

would indicate that solutions of salts in hydrazine should be good conductors of the electric current. It is definitely a basic solvent since it acts as an electron pair donor to coordinate with the proton to form the hydrazinium ion and with metallic ions to form complex ions.

Hydrazine is commercially available as the highly concentrated product containing 95% hydrazine and also as 85% hydrazine hydrate (57% N_2H_4). The latter can be dehydrated to give a product of high hydrazine content (better than 96%) by treatment with sodium hydroxide. Further dehydration to remove the last traces of water must be effected by distillation over sodium hydroxide or barium oxide. Care must be taken in the storage of hydrazine since it absorbs moisture and carbon dioxide from the air quite rapidly and is also susceptible to autoxidation, that is, to reaction with molecular oxygen. The latter reaction is catalyzed tremendously by traces of dissolved copper and leads to deterioration of hydrazine to form nitrogen and water (38).

Its solvent properties have been investigated only to a limited extent. Semi-quantitative solubility data are given in Table 33.

Hydrazine may be regarded as the parent substance of a solvent system of compounds. Analogous groups are listed in Table 34. For purposes of comparison, not only are the corresponding ammonio compounds given in this table, but also, since hydroxylamine derivatives

TABLE 34

SYSTEMS OF COMPOUNDS

A. Analogous Groups

HOH	OH	O	$\text{H}_2\text{O} \cdot \text{H}^+$
HNH_2	NH_2	$\text{NH}; \text{N}$	$\text{NH}_3 \cdot \text{H}^+$
HN_2H_3	N_2H_3	N_2H_2	$\text{N}_2\text{H}_4 \cdot \text{H}^+$
HNHOH	NHOH	NOH	$\text{NH}_2\text{OH} \cdot \text{H}^+$

B. Solvo Compounds

<i>Aquo Compounds</i>	<i>Ammono Compounds</i>	<i>Derived from</i>	
		<i>Hydrazine</i>	<i>Hydroxylamine</i>
KOH	KNH_2	KN_2H_3	$\text{KNHOH} (?)$
H_3O^+	NH_4^+	N_2H_5^+	$\text{NH}_2\text{OH} \cdot \text{H}^+$
CH_3OH	CH_3NH_2	$\text{CH}_3\text{N}_2\text{H}_3$	CH_3NHOH
$\text{C}_6\text{H}_5\text{OH}$	$\text{C}_6\text{H}_5\text{NH}_2$	$\text{C}_6\text{H}_5\text{N}_2\text{H}_3$	$\text{C}_6\text{H}_5\text{NHOH}$
$\text{R}_2\text{C}=\text{O}$	$\text{R}_2\text{C}=\text{NH}$	$\text{R}_2\text{C}=\text{N}_2\text{H}_2$	$\text{R}_2\text{C}=\text{NOH}$
$\text{RCH}=\text{O}$	$\text{RCH}=\text{NH}$	$\left\{ \begin{array}{l} \text{RCH}=\text{N}_2\text{H}_2 \\ (\text{RCH}=\text{N}-\text{N}=\text{CHR}) \end{array} \right\}$	$\text{RCH}=\text{NOH}$
$\text{CO}(\text{OH})_2$	$\left\{ \begin{array}{l} \text{CO}(\text{NH}_2)_2 \\ \text{C}(\text{NH})(\text{NH}_2)_2 \end{array} \right\}$	$\left\{ \begin{array}{l} \text{CO}(\text{N}_2\text{H}_3)_2 \\ \text{C}(\text{N}_2\text{H}_2)(\text{N}_2\text{H}_3)_2 \end{array} \right\}$	$\left\{ \begin{array}{l} \text{NH}_2\text{CO}(\text{NHOH})^* \\ \text{C}(\text{NH})(\text{NHOH})_2^* \end{array} \right\}$
$\text{SO}_2(\text{OH})_2$	$\left\{ \begin{array}{l} \text{NH}_2\text{SO}_2\text{OH} \\ \text{SO}_2(\text{NH}_2)_2 \end{array} \right\}$	$\left\{ \begin{array}{l} \text{N}_2\text{H}_3\text{SO}_2\text{OH} \\ \text{SO}_2(\text{N}_2\text{H}_3)_2 \end{array} \right\}$	HONHSO_2OH

* Oxyurea and dioxyguanidine, respectively.

are discussed very briefly in the following section of this chapter, compounds related to hydroxylamine as a parent substance of a system of acids, bases, and salts are also listed.

Since hydrazine salts furnish hydrazinium ions, they may be expected to behave as acids in anhydrous hydrazine; metallic hydrazides are formally the solvo bases of such a system. Only limited experimental studies have been made to extend these formal analogies to include related solvo acids, that is, compounds which are derived from hydrazine in the same way that ammonio acids are related to ammonia.

Hydrazine is an excellent electrolytic solvent. Data given in Table 35 indicate that conductance values resemble more closely those which characterize water than those which have been determined for the same salts in liquid ammonia. Hydrazine has a higher dielectric constant than ammonia. It has a slightly greater viscosity than water; values for the equivalent conductances of salts and for ionic mobilities are, therefore, generally somewhat lower in hydrazine than in aqueous solution.

Experimental evidence has been presented to demonstrate that the reaction between sodium hydrazide, serving as a base in anhydrous

TABLE 35
EQUIVALENT CONDUCTANCE OF ELECTROLYTES IN HYDRAZINE

<i>Electrolyte</i>	<i>0°C.</i>	Λ_{∞}	<i>In H₂O at 25°C.</i>
		<i>25°C.</i>	
KCl	86.2	130.3	150.6
KBr	134.9
KI	132.7
KClO ₄	129.6
NaI	114.5
KClO ₃	91.5
NaClO ₄	111.4
LiClO ₄	69.6
N ₂ H ₄ ·HCl	104.2	156.5	(134.4)
N(C ₂ H ₅) ₄ Cl	66.3	100.6	109.3
N(C ₂ H ₅) ₄ Br	105.3
N(C ₂ H ₅) ₄ I	68.1	102.9	109.8
N(C ₃ H ₇) ₄ I	64.0	95.9
N(C ₃ H ₇) ₄ ClO ₄	61.5	93.0
C ₆ H ₅ COOH·N ₂ H ₄	86.5

hydrazine, and hydrazine hydrochloride, representing an acid type solute (and furnishing the hydrazinium ion), can take place in accordance with the following equation:



or



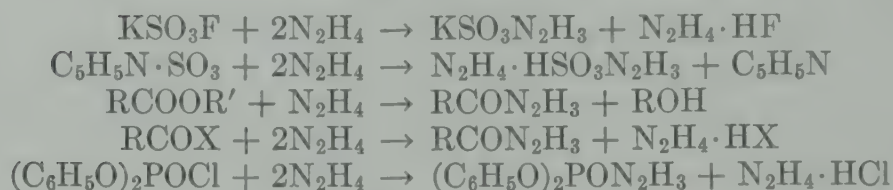
This is an example of a neutralization reaction involving the ionic species whose formation through self-ionization of the solvent defines the acid and base analogs.

Cadmium, zinc, and iron are displaced from solutions of their salts in anhydrous hydrazine on treatment with metallic sodium.* Reactions of solvation are also known. Hydrazine is an excellent coordinating agent. Anhydrous zinc sulfate, when added to anhydrous hydrazine, undergoes a slaking process with formation of the corresponding hydrazinate. Compounds containing an active halogen or ester group undergo solvolysis in anhydrous hydrazine. It is usually not necessary, however, to employ anhydrous hydrazine for this purpose since aqueous solutions of hydrazine function equally as well in converting compounds of this type into the corresponding hydrazine derivatives. Typical examples are listed in the following table.

* Reference should be made to the fact that compounds of bismuth, arsenic, copper, mercury, silver, lead, platinum, and palladium are reduced by hydrazine to the corresponding metals.

TABLE 36

SOLVOLYTIC REACTIONS INVOLVING HYDRAZINE



A complete discussion of the behavior of anhydrous hydrazine as a solvent and of the relationship of a wide variety of hydrazine derivatives to hydrazine as the parent substance is presented in considerable detail in Audrieth and Ogg's *The Chemistry of Hydrazine* (39).

HYDROXYLAMINE (40, 41)

A survey of the properties of hydroxylamine and of its various derivatives indicates that this substance may also be considered as the parent substance of a system of acids, bases, and salts. Liquid anhydrous hydroxylamine has been found to dissolve many substances quite readily. For example, potassium iodide, potassium cyanide, and potassium bromide are dissolved in large amounts, and sodium nitrate, barium nitrate, sodium chloride, and potassium chloride in lesser quantities. Sodium hydroxide, crystalline barium hydroxide, and ammonia are also very soluble. Peculiarly enough, solutions of barium nitrate and potassium sulfate in hydroxylamine, when mixed, are said to give no precipitate.

Although hydroxylamine is closely related to hydrazine and hydrogen peroxide and also to water and ammonia, from a chemical point of view, it is not a satisfactory substance to use as a solvent. It is a crystalline material which melts at 32°C. and is subject to explosive decomposition at higher temperatures. Like hydrazine, it is a basic material; it is extremely hygroscopic and tends to pick up carbon dioxide quite readily. It also suffers reaction with molecular oxygen, although the autoxidation phenomena have not been studied as thoroughly as they have for hydrazine. Hydroxylamine is a good complexing agent and forms a great many compounds with metallic salts containing hydroxylamine of crystallization. Since it is a good proton acceptor, forming the hydroxylammonium ion, it may be anticipated that compounds of this type would serve as acids in anhydrous hydroxylamine. Compounds related to hydroxylamine as the parent substance are presented formally in Table 34.

No experimental evidence to demonstrate the usefulness of the solvent system concept in the case of hydroxylamine has been presented. On the other hand, it should be pointed out that its consideration as a parent solvent does help to classify the large number of hydroxylamine derivatives which are known. There are three replaceable hydrogen atoms in hydroxylamine, indicating that there may exist six classes of derivatives corresponding to the type formulas: XNHOH , H_2NOX , X_2NOH , XNHOX , X_2NOX , and X_3NO . Among the inorganic compounds, only analogs of sulfuric acid, carbonic acid, nitrous acid and nitric acid are known. Such substances as hydroxylaminosulfonic acid, HONHSO_3H , nitrohydroxylamic acid, $\text{HO}(\text{NO})\text{NOH}$ (which is known only in the form of its salts), hyponitrous acid, HONNOH (which may be regarded as the oxime of nitrous acid), and nitrosohydroxylamine, $\text{HON}(\text{NO})\text{H}$ (better known as the parent substance of the isonitramines), may be considered as solvo acid derivatives of hydroxylamine. Reference should also be made to the fact that fulminic acid, HONC , is generically related to hydroxylamine in the same way that hydrocyanic acid is to ammonia.

LIQUID HYDROGEN CYANIDE (42)

Although the poisonous character of hydrogen cyanide has been a deterrent to its extensive investigation, sufficient data have been accumulated to demonstrate that this substance does possess interesting properties as a solvent medium and may be treated successfully as a parent substance of a system of acids, bases, and salts.

In the laboratory hydrogen cyanide is readily obtained by treatment of sodium cyanide with dilute sulfuric acid. For use as a solvent in exact experimental work, the material is purified by repeated distillation and condensation over phosphorus(V) oxide. Some important physical constants of the pure substance are given in Table 37.

TABLE 37

SOME PHYSICAL CONSTANTS OF ANHYDROUS HYDROGEN CYANIDE

<i>Property</i>	<i>Value</i>
Freezing point, °C.	-13.35
Boiling point, °C.	25.0
Density, grams/cc.	0.681 (25°C.)
Viscosity, centipoise	0.201 (20.2°C.)
Dielectric constant	123 (15.6°C.)
Specific conductance, ohm ⁻¹	5.0×10^{-7} (0°C.)
Ion product, $(\text{H} \cdot \text{HCN}^+)(\text{CN}^-)$	ca. 2×10^{-19} (12°C.)

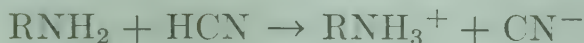
Although a large number of inorganic salts are soluble in liquid hydrogen cyanide, its solvent power is much inferior to that of water. This observation emphasizes the fact that the dissolving power of a solvent is not necessarily related directly to its dielectric constant, but depends also on other factors. Available qualitative solubility (and also conductivity) relationships are summarized in Table 38.

TABLE 38
QUALITATIVE SOLUBILITIES IN LIQUID HYDROGEN CYANIDE

Readily Soluble; Non-conductors	Soluble; Poor Conductors	Soluble; Fair Conductors	Soluble; Good Conductors	Slightly Soluble	Insoluble
I ₂ H ₂ O SnCl ₄ SnBr ₄ SnI ₄ S ₂ Cl ₂	HC ₂ H ₃ O ₂ H ₂ SO ₄ HNO ₃ AsCl ₃ SbCl ₃	HCl AgNO ₃ (reacts) Ag ₂ SO ₄ (reacts) BiCl ₃ POCl ₃ SOCl ₂ SO ₂ Cl ₂	LiCl LiBr LiI LiSCN LiClO ₄ LiNO ₃ NaBr NaI NaSCN NaClO ₄ NaNO ₃ KCl KBr KI KCN KCNO (reacts) KSCN KClO ₄ KNO ₃ KHSO ₄ K ₂ CrO ₄ RbCl CsCl AgClO ₄ FeCl ₃ SbCl ₅	NaCl Na ₂ B ₄ O ₇ K ₂ SO ₃ K ₂ SO ₄ NH ₄ Cl AgCN AgCNO Cu ₃ (AsO ₄) ₂ CdI ₂ HgCl ₂ HgBr ₂ CoCl ₂ As ₂ O ₃ H ₃ BO ₃	CaCl ₂ Ca(NO ₃) ₂ SrCl ₂ Sr(NO ₃) ₂ BaCl ₂ Ba(NO ₃) ₂ CuCN CuSO ₄ AgCl AgI Hg ₂ Cl ₂ HgI ₂ HgO AlCl ₃ SnCl ₂ PbCl ₂ PbBr ₂ PbI ₂ P ₄ O ₁₀ Cr ₂ O ₃

Liquid hydrogen cyanide is an excellent solvent for organic compounds. Alcohols, ethers, ketones, monobasic acids, acid halides, ni-

trogen bases, and many other classes of organic materials are soluble. Most nitrogen bases yield conducting solutions as a result of the following reaction:



Quantitative conductivity measurements have shown that typical alkali metal salts (for example, halides, thiocyanates, perchlorates, nitrates) are strong electrolytes in anhydrous hydrogen cyanide. Ionic mobilities in this solvent at 18°C. (Table 39), are three to four times greater than the values for corresponding ions in water.

TABLE 39

IONIC MOBILITIES IN HYDROGEN CYANIDE AT 18°C.

<i>Ion</i>	<i>HCN</i>	<i>H₂O</i>
Li ⁺	135.5	33
Na ⁺	132.4	43
K ⁺	151.4	64
Rb ⁺	153.2	67
Cs	158.2	68
Cl ⁻	210.0	65
Br ⁻	211.4	67
I ⁻	212.5	67
NO ₃ ⁻	201.4	62
ClO ₄ ⁻	203.4	56
CNS ⁻	205.3	57

Even though hydrogen cyanide has a much lower viscosity than water, such high mobilities indicate that ions are not solvated (or very much less so than in water). Indeed few, if any, true solid solvates are known. Conductivity and cryoscopic studies show that sulfuric acid and trichloroacetic acid, typical strong acids in water, are very weak electrolytes in hydrogen cyanide.

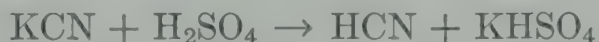
It has been proposed that liquid hydrogen cyanide undergoes auto-ionization in accordance with the following equilibrium:



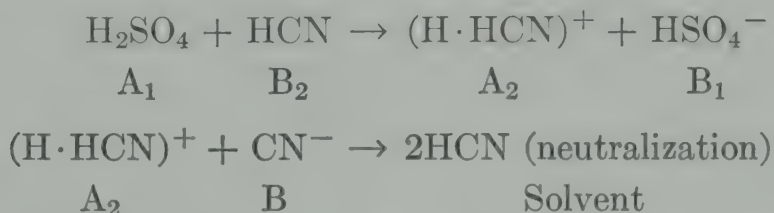
Substances capable of releasing the proton to the solvent are regarded as acids, whereas metal cyanides, or substances capable of reacting with the solvent to give the cyanide ion (for example, amines), are considered to be bases. A brief discussion of typical reactions which have been explained in terms of acid-base phenomena follows.

A number of reactions which may be regarded as typical neutralization reactions have been studied. For example, when potassium

cyanide in liquid hydrogen cyanide is treated with sulfuric acid in the formula weight ratio of 1:1, no apparent reaction takes place. Evaporation in vacuo of the resulting solution yields practically the calculated quantity of potassium hydrogen sulfate, indicating that the following over-all reaction has taken place:



This reaction may also be represented by equilibria following the Brönsted-Lowry notation:



Reaction between the cyanide and sulfuric acid in a 2:1 molar ratio produces practically the theoretical quantity of the slightly soluble potassium sulfate. The potassium cyanide-sulfuric acid system has also been studied both conductometrically and potentiometrically. In each case, inflection points corresponding to the formation of the acid and normal sulfates are obtained. A summary of some of the acid-base systems studied conductometrically is given in Table 40.

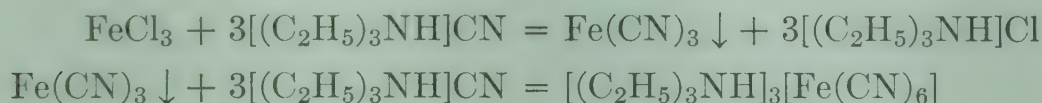
TABLE 40
ACID-BASE SYSTEMS IN LIQUID HYDROGEN CYANIDE

<i>Acid</i>	<i>Base</i>	<i>Salts Formed</i>
H ₂ SO ₄	KCN	KHSO ₄ ; K ₂ SO ₄
H ₂ SO ₄	(C ₂ H ₅) ₃ N	[(C ₂ H ₅) ₃ N · H]HSO ₄ ; [(C ₂ H ₅) ₃ N · H] ₂ SO ₄
H ₂ SO ₄	C ₃ H ₇ NH ₂	[C ₃ H ₇ NH ₂ · H]HSO ₄ ; [C ₃ H ₇ NH ₂ · H] ₂ SO ₄
H ₂ SO ₄	C ₅ H ₅ N	[C ₅ H ₅ N · H]HSO ₄ ; [C ₅ H ₅ N · H] ₂ SO ₄
HCl	(C ₂ H ₅) ₃ N	[(C ₂ H ₅) ₃ N · H]Cl; [(C ₂ H ₅) ₃ N · H]Cl · HCl
HCl	C ₅ H ₅ N	[C ₅ H ₅ N · H]Cl
CHCl ₂ COOH	KCN	CHCl ₂ COOK; CHCl ₂ COOK · CHCl ₂ COOH; CHCl ₂ COOK · 2CHCl ₂ COOH
CHCl ₂ COOH	(C ₂ H ₅) ₃ N	[(C ₂ H ₅) ₃ N · H](OOCCHCl ₂); [(C ₂ H ₅) ₃ N · H](OOCCHCl ₂) · CHCl ₂ COOH

Although most of the common acid-base indicators are soluble in liquid hydrogen cyanide, they appear to be of doubtful value for the study of acid-base relationships. Many indicators do not give substantial color changes when sulfuric acid is employed as solute, demonstrating that sulfuric acid is weakly acidic in liquid hydrogen cyanide. Inasmuch as typical bases (that is, CN⁻ ion and amines) cause

liquid hydrogen cyanide to turn brown, the colors of indicators in such solutions soon become masked.

A number of metal cyanides undergo reactions which may be reasonably interpreted in terms of amphoteric behavior. The addition of triethylamine to a solution of an iron(III) salt results in the precipitation of the metal cyanide, which dissolves in an excess of the base. The stoichiometry of the changes which occur has been verified by potentiometric titration:



The analogy between this sequence of reactions and that involved in the precipitation and dissolution of aluminum hydroxide by means of sodium hydroxide solution is apparent.

Silver and mercury(II) cyanides behave in a similar manner. Thus treatment of a silver perchlorate solution with triethylamine gives a precipitate of silver cyanide. This substance is soluble in either a hydrogen cyanide solution or sulfuric acid or excess triethylamine; solution in the triethylamine yields the compound $[(\text{C}_2\text{H}_5)_3\text{NH}][\text{Ag}(\text{CN})_2]$. Mercury(II) cyanide reacts with potassium cyanide to give either $\text{K}[\text{Hg}(\text{CN})_3]$ or $\text{K}_2[\text{Hg}(\text{CN})_4]$.

Several silver salts, for example, the nitrate, phosphate, sulfate, and cyanate, undergo extensive solvolysis in liquid hydrogen cyanide. In each case, silver cyanide is precipitated from solution. It has been shown that the solvolysis of silver nitrate or sulfate may be inhibited by the addition of the parent acid, that is, nitric or sulfuric acid. Silver iodide, which is insoluble in liquid hydrogen cyanide, is not solvolyzed even on long standing. On the other hand, the insoluble cyanate is slowly converted to silver cyanide. Of the various silver salts tested, only the perchlorate undergoes no apparent solvolysis. It is interesting in this connection to point out that this indicates that perchloric acid possesses considerably greater acid character in liquid hydrogen cyanide than do either nitric acid or sulfuric acid.

Acid chlorides of the type RCOCl are readily solvolyzed:



The reaction is driven toward completion by the addition of the base pyridine, which combines with the hydrogen chloride. The pyridinium chloride thus formed is precipitated from solution by the addition of anhydrous ether. Fractionation of the resulting ethereal solution gives

the desired acid cyanide. Acetyl cyanide (20% yield) and benzoyl cyanide (80% yield) have been obtained in this manner.

ACETONITRILE

Some physical constants of pure acetonitrile, CH_3CN , the methyl derivative of hydrogen cyanide, are given in Table 41.

TABLE 41

SOME PHYSICAL CONSTANTS OF ANHYDROUS ACETONITRILE

<i>Property</i>	<i>Value</i>
Freezing point, °C.	-41
Boiling point, °C.	81.6
Density, grams/cc.	0.783 (20°C.)
Viscosity, centipoise	0.345 (25°C.)
Dielectric constant	36 (20°C.)
Specific conductance, ohm ⁻¹	$5-9 \times 10^{-8}$ (25°C.)

Acetonitrile is an excellent solvent for many inorganic substances; data are given in Table 42. A number of solvates (for example, $\text{CuCl}_2 \cdot$

TABLE 42

QUALITATIVE SOLUBILITIES OF INORGANIC SUBSTANCES IN ACETONITRILE

<i>Readily Soluble</i>		<i>Soluble</i>	<i>Slightly Soluble</i>	<i>Relatively Insoluble</i>
Cl_2	ZnCl_2	NaSCN	NH_4NO_3	NH_4Br
Br_2	CdI_2	NaI	LiCl	KNO_3
I_2	$\text{Hg}(\text{CN})_2$	KI	NaCl	KCl
HCl	HgCl_2	KMnO_4	NaBr	$\text{KC}_2\text{H}_3\text{O}_2$
HBr	$\text{Pb}(\text{ClO}_4)_2$	RbI	CsI	RbSO_3NH_2
HI	BiCl_3	CuBr	CuCl_2	Hg_2Cl_2
NH_3	FeCl_2	CdCl_2	$\text{Ca}(\text{NO}_3)_2$	$\text{Pb}(\text{NO}_3)_2$
H_2S	FeBr_2	CdBr_2	CaCl_2	PbCl_2
SO_2	FeCl_3	HgBr_2	HgI_2	$\text{Pb}(\text{SO}_3\text{NH}_2)_2$
NH_4SCN	FeBr_3	AlCl_3	PbI_2	
LiBr		SnCl_2	$\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$	
KSCN		SnCl_4	BiI_3	
CuCl		BiBr_3		
CuBr_2		CoCl_2		
AgNO_3		CoBr_2		

$2\text{CH}_3\text{CN}$, $\text{CuBr}_2 \cdot \text{CH}_3\text{CN}$, $\text{Ca}(\text{NO}_3)_2 \cdot \text{CH}_3\text{CN}$, $\text{ZnCl}_2 \cdot 2\text{CH}_3\text{CN}$, $\text{CoCl}_2 \cdot 3\text{CH}_3\text{CN}$) have been isolated; these compounds are often very unstable in air and either decompose directly or absorb moisture readily.

Salts may be divided into three groups on the basis of their conductivity behavior in acetonitrile: (a) "strong" electrolytes, including tetra-substituted ammonium halides, silver and potassium picrates and potassium iodide; (b) "moderately strong" electrolytes, including picrates, bromides, and iodides of incompletely substituted ammonium bases, lithium and sodium picrates, and silver nitrate; and (c) "weak" electrolytes, the chlorides of incompletely substituted ammonium bases (43).

For salts containing a common anion, the following order of increasing conductance is observed:



For salts of a common cation, the order is:



For quaternary ammonium salts, the square-root law holds, that is, a plot of equivalent conductance versus square root of concentration yields a straight line in the concentration range (up to 5×10^4 liters per mole) studied.

The relative electrode potentials (Table 43) of a number of half cells have been obtained from measurements of the system: M/0.01 *N*

TABLE 43

POTENTIALS IN ACETONITRILE AT 25°C.

(System: M/0.01 *N* MX in CH₃CN/0.01 *N* AgNO₃ in CH₃CN/Ag)

<i>Half Cell</i>	<i>Emf. of Cell, volts</i>
Li/LiCl	2.476
K/KI	2.3443
Rb/RbI	2.3275
Cs/CsI	2.2723
Na/NaI	2.2592
Ca/Ca(NO ₃) ₂	2.140
Zn/ZnCl ₂	0.975
Cd/CdI ₂	0.7031
Cu/CuCl	0.6065
Pb/Pb(ClO ₄) ₂	0.3544
Pt, H ₂ /HCl	0.2324
Hg/HgBr ₂	0.0231

MX in CH₃CN/0.01 *N* AgNO₃ in CH₃CN/Ag (44). Dilution of the electrolyte in the half cells tested had, with the exception of lead(II) nitrate and hydrogen chloride, relatively little effect on the emf. of the

cell. The values for the potentials indicate that copper can displace hydrogen and lead from their compounds dissolved in acetonitrile.

Attempts to electrodeposit some of the more active metals from the respective salt solutions in acetonitrile have proved unsuccessful. Electrolysis of solutions of lithium nitrate, magnesium bromide, and aluminum perchlorate results in the decomposition of the solvent at potentials below those found for the metals against such solutions (45, 46). Silver, however, is deposited from a solution of the nitrate at a constant potential of 1.15 volts (45).

In addition to forming solvates with inorganic salts (p. 140), acetonitrile enters into other combinations which may be interpreted in terms of acid-base behavior. Thus conductivity curves of the system acetonitrile-picoline (mixture of isomers) at 0°, 25°, and 50°C. have a sharp maximum at about 85 mole per cent acetonitrile (47). When the mixtures characterized by maximum conductivity are electrolyzed between a silver anode and a platinized platinum cathode, the anode is dissolved and ethane is liberated at the cathode. It may be assumed that acetonitrile behaves (in the Lewis sense) as an acid toward the picolines:



The cation discharged during electrolysis dissociates into B and CH₃; two methyl radicals then combine to form ethane. Indicators having color transitions in water above pH 5 show acid reactions in acetonitrile, and basic reactions when the picolines are added.

Acetonitrile is also capable of acting as a basic solvent. It combines directly with such Lewis acids as boron trifluoride and boron trichloride to yield monosolvates (48). Vapor density measurements show that these solvates are practically completely dissociated in the vapor state. In dilute solution in acetonitrile, CH₃CN:BF₃ is not appreciably dissociated.

Acetonitrile also forms addition compounds with various hydrogen acids. Compounds corresponding to the formulas [RCN:H]Cl and [RCN:H]Cl·HCl have been prepared by passing the hydrogen halide into the nitrile dissolved in anhydrous ether or benzene (49). These compounds decompose readily, the chlorides being most labile and the iodides most stable. The relative acid strengths of a number of hydrogen acids based upon the equilibrium



have been determined (50, 51). Acids have been arranged in Table 44 in order of their relative strengths, as established by the indicator method (51).

TABLE 44

ORDER OF DECREASING ACID STRENGTH IN ACETONITRILE

<i>o</i> -Toluidinium ion	Mandelic acid
Bromphenol blue, colorless-yellow	Glycolic acid
β -Naphthalenesulfonic acid	Monochloroacetic acid
Picric acid	Piperidinium ion
Neutral red	<i>o</i> -Chlorobenzoic acid
Dichloroacetic acid	Isoamylammonium ion
β -Dinitrophenol	<i>o</i> -Toluic acid
Bromophenol blue, yellow-blue	Benzoic acid
Diphenylguanidinium ion	Acetic acid
α -Dinitrophenol	

Strong acids such as perchloric acid can be titrated quantitatively with diphenylguanidine, with dimethyl yellow, benzoyl auramine, or thymol blue used as indicators. For weak acids, such as acetic acid, bases of sufficient strength are not available for use in titration.

Little has been done towards evaluating acetonitrile as a medium for inorganic chemical reactions. The formation of solvates has already been mentioned. A few metathetical and oxidation-reduction reactions have been described (52). Treatment of an acetonitrile solution of copper(II) chloride or bromide with hydrogen sulfide results in the formation of the soluble metal sulfide and the appropriate halogen halide. Silver chloride precipitates upon treatment of the metal nitrate with copper(II) chloride. Reaction between copper(II) salts and hydrogen iodide or sodium iodide yields molecular iodine and copper(I) iodide. Copper(II) chloride oxidizes tin(II) chloride to the tetrachloride. Copper(I) as chloride or bromide is converted to the dipositive state by the action of the respective free halogen.

FORMAMIDE AND ACETAMIDE

Walden (53) was the first to point out the very interesting properties of these two substances as electrolytic solvents. The physical properties of both are summarized in Table 45.

Both amides have higher dielectric constants than the related carboxylic acids, formic and acetic acid, from which they are derived. The trend is not quite so clear in making reference to their relationship with hydrogen cyanide and acetonitrile. Formamide possesses a convenient liquid range, but is somewhat difficult to prepare in the

TABLE 45

PHYSICAL PROPERTIES

	<i>Formamide</i>	<i>Acetamide</i>
Melting point, °C.	2°	81°
Boiling point, °C.	193°	222°
Dielectric constant	84 (20°C.)	59.2 (83°C.)
Viscosity, in millipoises	7.68 (105°C.)	13.2 (105°C.)
Specific gravity, 20°/4°C.	1.139	1.159

pure state. Acetamide, on the other hand, is a solvent which can be used only at higher temperatures. Although both substances have high dielectric constants, it is significant that each possesses a relatively high viscosity, with the result that ionic mobilities and conductance values are correspondingly low (37, 54, 55).

No quantitative solubility data are available. Formamide has been found to dissolve a member of alkali metal salts and to decompose salts of weak acids such as zinc cyanide, which dissolves with the liberation of hydrogen cyanide (56, 57). It also forms complex basic salts with copper, cobalt, nickel, and zinc. Solvo-basic salts are formed when formamide reacts with the bismuth and antimony halides and with mercury(II) compounds (58).

Acetamide dissolves such compounds as potassium chloride, potassium iodide, potassium cyanide, and mercuric chloride (37). A more extended investigation of acetamide as a solvent was undertaken by Stafford (59), but only a summary of his results has been published. In emphasizing the solvent character of acetamide, Stafford writes:

"It [acetamide] contains a methyl group which should give it solvent powers for hydrocarbons; its carbonyl group relates it to ketones, esters, and acids; its tautomeric hydroxyl group gives it kinship to water and the alcohols; its amino group brings it into line with ammonia and its derivatives, while the ease with which it yields nitrile suggests a relationship to cyanogen compounds. . . . In the field of inorganic chemistry, the above considerations are supplemented by the fact that acetamide outranks all but a half a dozen substances in the magnitude of its dielectric constant."

Of 400 organic compounds, he says:

"The only one [organic compound] showing no indication of solubility was cellulose. Asparagine, barbituric acid, oxamide, and uric acid are sparingly soluble at low temperatures, that is, below 100°C. It is significant that these same substances are but slightly soluble in

water and are rated as insoluble in alcohol and ether. . . . [Among the organic compounds] sixty-five ammonia-nitrogen derivatives, seventeen carbohydrates (excepting cellulose but including starch), sixty-eight dyestuffs, forty-four alcohols, eleven nitro and nitroso compounds and a number of miscellaneous nitrogen derivatives, all dissolve readily. Of the twenty hydrocarbons tested, anthracene, phenanthrene, and triphenylmethane are quite soluble. . . . Forty-five acids tested are all soluble, but those with very long hydrocarbon chains are less soluble than others. . . . Some twenty oxygen compounds were tested, in this class the ethers appearing to be less soluble than the others.

"The solubilities of inorganic compounds are strikingly analogous to those in water. Exceptions are presented by potassium perchlorate, the halides of mercury and lead, and the phosphate and oxide of mercury, all of which are more soluble in acetamide than in water. . . . Among the inorganic compounds bismuth nitrate gives a white insoluble compound similar to that formed by hydrolysis or ammonolysis. Mercurous nitrate undergoes sudden transformation in contact with the solvent. A similar action appears to take place with mercurous halides. Chromates are slowly reduced in acetamide solutions although even the solution of chromium trioxide (which in color exactly resembles solutions of chromates) is stable for quite a while."

Stafford also investigated metathetical reactions in acetamide solution and states that the "precipitates in acetamide are even similar in appearance to those formed in water, colored sulfides, for example, appearing precisely as when precipitated from water."

The possible usefulness of formamide and acetamide as solvents for the electrodeposition of metals has also been investigated (57). Metallic deposits are obtained from formamide solutions at 100°C., using the following compounds as electrolytes: zinc cyanide, cadmium cyanide, lead nitrate, tin(IV) iodide, ammonium hexachlorostannate, cobalt(II) acetate, nickel(II) acetate, and hexammine nickel(II) bromide. Previous attempts to deposit magnesium, aluminum, and iron from solutions of their respective chlorides in formamide were unsuccessful, although reference is made in this earlier study (56) to the fact that solutions of lead nitrate, lead chloride, copper(II) sulfate, copper(I) chloride, zinc oxide, zinc chloride, and tin(II) chloride were electrolyzed to yield metallic deposits.

In electrodeposition of metals from acetamide at 100°C. metallic deposits were obtained when the following substances were used as solutes: zinc cyanide, cadmium cyanide, tin(IV) iodide, ammonium

hexachlorostannate, lead chloride, hexammine nickel(II) bromide, cobalt(II) chloride, and iron(II) acetate. No success was achieved in the electrolysis of solutions of trivalent cobalt complexes such as hexammine cobalt(III) chloride and potassium hexacyanocobaltate(III).

Both formamide and acetamide are highly associated solvents as has been pointed out by Copley, Zellhoefer, and Marvel (60) in their work dealing with the influence of structure and substitution on hydrogen bonding ability. Both these substances are relatively poor hydrogen bonding agents simply because they are so highly associated. If, however, one or both of the hydrogen atoms on the amide nitrogen atom are replaced by alkyl groups, the ability of the resulting compounds to serve as hydrogen bonding agents is increased tremendously. One of the more useful of the newer solvents is dimethyl formamide, which is a good hydrogen bonding agent, particularly for organic compounds which contain an active hydrogen. If, however, association of the compounds through hydrogen bonding with itself is reduced by substituting alkyl groups for hydrogen atoms, one would expect the resulting compounds to be poorer solvents for inorganic compounds even though better solvents for organic compounds. An investigation of the change in electrochemical characteristics of these substances as solvents, as a function of the nature of the substituent on the nitrogen atom, would undoubtedly clarify this whole matter.

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ACETIC ACID

Although anhydrous acetic acid was employed as a solvent for cryoscopic measurements by Raoult as far back as 1884 (1), the use of this material as a medium for chemical reactions has been developed primarily within the last thirty years. The first extensive compilation of the physical and chemical properties of anhydrous acetic acid was published in 1924 in Walden's classic *Elektrochemie Nichtwässriger Lösungen* (2).

Acetic acid, the most important commercial organic acid, is readily available as the "glacial" product of greater than 99% purity. Conversion to the anhydrous material is a relatively simple matter and involves essentially removal of water by reaction with some agent such as acetic anhydride or triacetyl borate (3, 4). Fractionation, after such treatment, gives a product of a high purity as determined by its freezing point or specific conductivity. The relative ease with which the pure acid may be obtained and the fact that it may be handled without elaborate precautions (little moisture is absorbed upon exposure to the atmosphere for short intervals) undoubtedly account in great part for the extensive work that has been performed in this solvent.

The physical properties of the anhydrous acid are summarized in Table 46.

TABLE 46
SOME PHYSICAL CONSTANTS OF ACETIC ACID

<i>Property</i>	<i>Value</i>	<i>Reference</i>
Freezing point, °C.	16.7	(5)
Boiling point, °C.	118.1	(5)
Specific conductivity, ohm ⁻¹	$0.5-0.8 \times 10^{-8}$ (25°C.)	(6)
Specific gravity	1.05605 (15°/15°C.)	(6)
$K = [\text{H} \cdot \text{HC}_2\text{H}_3\text{O}_2^+] \times [\text{C}_2\text{H}_3\text{O}_2^-]$	2.5×10^{-13}	(6)
Dielectric constant	ca. 6 (25°C.)	(7)

Solutions in acetic acid can be studied over a wide and convenient liquid range. The acid exhibits a degree of dissociation of the same

order of magnitude as does water. As indicated by its rather low dielectric constant acetic acid is a better solvent for convalent than for ionic substances. Furthermore, the effect of interionic attraction must be large for solutions of electrolytes. These generaliaztions, based upon the physical properties of acetic acid, are borne out by studies of its solvent properties.

SOLVENT PROPERTIES

SOLUBILITY OF SALTS. The excellence of anhydrous acetic acid as a solvent for organic compounds is too well known to need further elaboration. Investigations of the solubilities of inorganic salts have been fairly extensive and have brought to light some interesting relationships. A rather comprehensive study, of a qualitative nature, of the solubility of common salts at room temperature has been carried out by Davidson (8). The results of this investigation are summarized in Table 47. The data indicate that practically all salts that are

TABLE 47

QUALITATIVE SOLUBILITIES OF SALTS IN ANHYDROUS ACETIC ACID

Readily Soluble	Less Soluble	Less Than One Part in 100	Insoluble	
LiNO ₃	AgNO ₃	NaCl	AgCl	Sulfates of
NH ₄ NO ₃	AlCl ₃	KCl	AgBr	Li
Ca(NO ₃) ₂	CoCl ₂	NH ₄ Cl	AgI	K
Cu(NO ₃) ₂	HgCl ₂	BaCl ₂	AgCN	Mg
CaCl ₂	HgI ₂	KBr	AgSCN	Ca
ZnCl ₂		NH ₄ Br	PbCl ₂	Ba
FeCl ₃		KI	PbI ₂	Cd
SbCl ₃		NH ₄ I	Hg ₂ Cl ₂	Zn
BaI ₂		NaNO ₃	CdI ₂	Hg(I)
ZnI ₂		KNO ₃	Ba(NO ₃) ₂	Hg(II)
KCN		KClO ₃	Ca ₃ (PO ₄) ₂	Al
NH ₄ SCN		Na ₂ SO ₄	Cu ₃ (PO ₄) ₂	Pb
LiC ₂ H ₃ O ₂		(NH ₄) ₂ SO ₄	CaCO ₃	Ag
KC ₂ H ₃ O ₂		Cu(C ₂ H ₃ O ₂) ₂		Cu
NH ₄ C ₂ H ₃ O ₂				Mn
Pb(C ₂ H ₃ O ₂) ₂				Fe(II)
Cd(C ₂ H ₃ O ₂) ₂				Fe(III)
				Co
				Ni

difficultly soluble in water are [with the exception of mercury(II) iodide] insoluble in acetic acid. However, solubility in water does not ensure solubility in acetic acid.

In addition to the qualitative information presented in Table 47, extensive quantitative data exist on the solubility of nitrates, halides, and acetates. These data are summarized in Tables 48, 49, and 50. The solubility behavior of the metal acetates in acetic acid is very similar to that of the hydroxides (their analogs) in water. In both solvents, with few exceptions, there is an enormous variation in solubility from the very soluble alkali metal compounds, on the one hand,

TABLE 48
SOLUBILITY OF NITRATES IN ANHYDROUS ACETIC ACID AT 25°C. (9)

Salt	Solubility in HC ₂ H ₃ O ₂		Solubility in H ₂ O
	Mole per Cent	Moles per 1000 g. Solvent	Moles per 1000 g. Solvent
Ba(NO ₃) ₂	0.0005	0.00008	0.400
KNO ₃	0.105	0.0175	3.74
NaNO ₃	0.121	0.0202	10.80
AgNO ₃	0.020	0.0033	14.00
NH ₄ NO ₃	0.370	0.0619	26.98
LiNO ₃		1.49 (30°C.)	
Ca(NO ₃) ₂ ·3HC ₂ H ₃ O ₂		1.41 (30°C.)	

TABLE 49
SOLUBILITY OF HALIDES IN ANHYDROUS ACETIC ACID AT 30°C. (10)

<i>Salt</i>	<i>Mole Per Cent</i>	<i>Moles per 1000 g. of Solvent</i>
CuCl ₂	0.0070	0.0012
NaCl	0.075	0.0125
NH ₄ Cl	0.080	0.0133
KCl	0.175	0.0292
BaCl ₂	0.0077	0.0013
SrCl ₂	5.12	0.899
HgCl ₂ ·2HC ₂ H ₃ O ₂	0.936	0.157
HgBr ₂	0.284	0.047
HgI ₂	0.011	0.0018

TABLE 50

SOLUBILITY OF ACETATES IN ANHYDROUS ACETIC ACID AT 25°C. (11)

<i>Metal</i>	<i>Solvates Isolated</i>	<i>Solubility, Mole Per Cent</i>
Li	$\text{LiC}_2\text{H}_3\text{O}_2 \cdot \text{HC}_2\text{H}_3\text{O}_2$	9.37
Na	$\text{NaC}_2\text{H}_3\text{O}_2 \cdot 2\text{HC}_2\text{H}_3\text{O}_2$ and $\text{NaC}_2\text{H}_3\text{O}_2 \cdot \text{HC}_2\text{H}_3\text{O}_2$	7.06
K	$\text{KC}_2\text{H}_3\text{O}_2 \cdot 2\text{HC}_2\text{H}_3\text{O}_2$ and $\text{KC}_2\text{H}_3\text{O}_2 \cdot \text{HC}_2\text{H}_3\text{O}_2$	12.29
NH_4	$\text{NH}_4\text{C}_2\text{H}_3\text{O}_2 \cdot \text{HC}_2\text{H}_3\text{O}_2$	23.46
Tl(I)	$\text{TlC}_2\text{H}_3\text{O}_2 \cdot \text{HC}_2\text{H}_3\text{O}_2$	ca. 2
Ca	$\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{HC}_2\text{H}_3\text{O}_2$	0.068
Sr	$\text{Sr}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{HC}_2\text{H}_3\text{O}_2$	4.81 (12)
Ba	$\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{HC}_2\text{H}_3\text{O}_2$ and $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{HC}_2\text{H}_3\text{O}_2$	3.48
Zn	None	0.0018
Pb(II)	None	31.9
	$\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 0.5\text{HC}_2\text{H}_3\text{O}_2$	19.72 (30°C.) (13)
Fe(III)	None	0 (practically)
Cu	$\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{HC}_2\text{H}_3\text{O}_2$	0.166
Ag	None	0.094 (76°C.)

to the very insoluble compounds of the less electropositive elements, on the other. Such a variation has been found by Kendall and co-workers (14, 15, 16) to be general in several systems of the type $\text{HX}:\text{MX}$. An explanation for this regularity is offered in terms of solvate formation, since this tendency seems to accompany high solubility. It is readily apparent from the data of Table 50 that this explanation holds true for metal acetate-acetic acid systems, with the behavior of lead(II) acetate at 25°C. being a notable exception.

NEUTRAL SALT EFFECTS ON SOLUBILITIES. The effect of added salts in increasing the solubility product of other salts in anhydrous acetic acid is quite marked. This effect is ordinarily much greater in acetic acid than in water, since activity coefficients of electrolytes decrease more rapidly with increasing concentration in the former solvent, owing to its low dielectric constant (17).

In a study of the solubility of potassium perchlorate in anhydrous acetic acid in the presence of ammonium perchlorate, sodium nitrate, and sodium bromide, and also of the solubility of potassium nitrate in the presence of ammonium chloride and nitrate, Seward and Hamblet (18) obtained data which agree with those predicted by the interionic attraction theory, provided a sufficiently large ion diameter is assumed. The conclusion was reached that the explanation of the properties of salt solutions in acetic acid medium requires that properties of the solvent in addition to its dielectric constant must be considered. Similar results were obtained by Scholl, Hutchison and Chandlee (19).

In an investigation of the system $\text{AgNO}_3\text{--NH}_4\text{NO}_3\text{--HC}_2\text{H}_3\text{O}_2$ over a temperature range of 40° to 90°C . Davidson and Geer (20) observed that in those regions in which the single nitrates occur as solid phases, the solubility of each increases with increasing ionic strength. These investigators also studied the system $\text{AgNO}_3\text{--LiNO}_3\text{--HC}_2\text{H}_3\text{O}_2$.

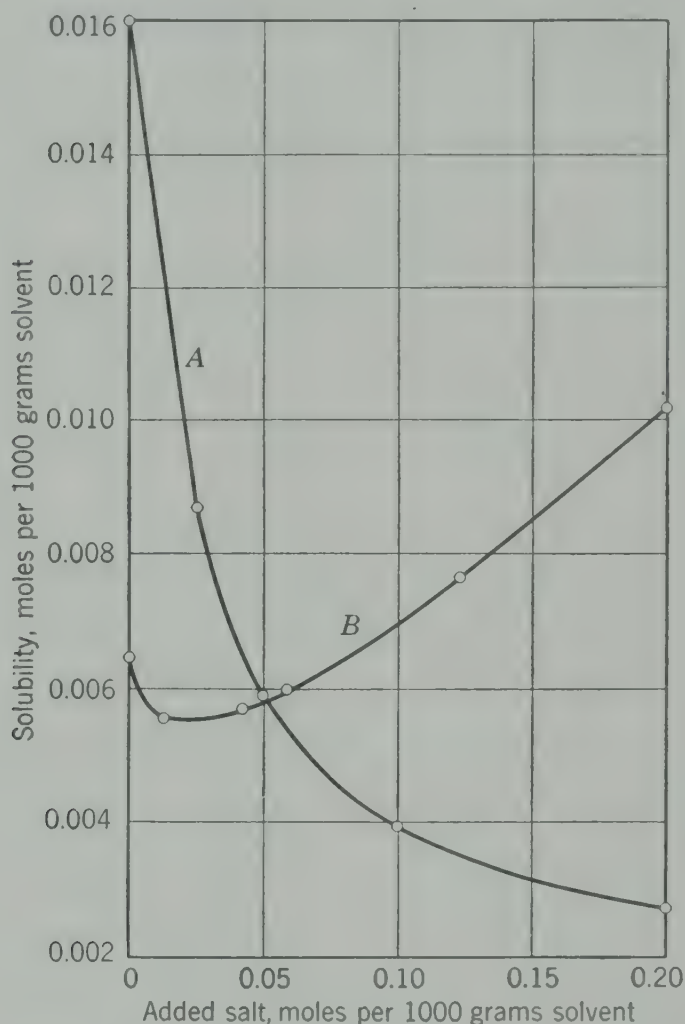


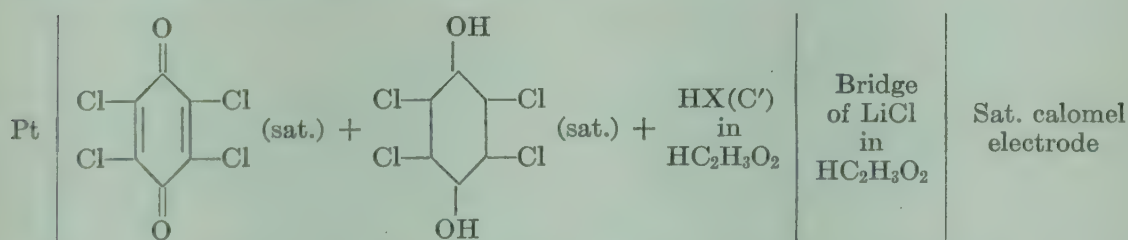
FIGURE 13. Combined common ion and salt effects on solubility. (A) TlCl in aqueous KCl solution at 25°C . (B) AgNO_3 in acetic acid solutions of LiNO_3 at 30°C .

The pertinent solubility data are depicted graphically in Figure 13. It is noteworthy that in acetic acid solutions, the effect of the common ion in depressing the solubility of silver nitrate is of minor significance compared with the neutral salt effect. Data for the $\text{TlCl--KCl--H}_2\text{O}$ system (17) are also presented on Figure 13. Although the experimental data demonstrate quite clearly the marked neutral salt effect in anhydrous acetic acid, it can scarcely be said that these results have been explained satisfactorily on an entirely theoretical basis.

GENERAL ACID-BASE RELATIONSHIPS IN ACETIC ACID

Acid-base relationships in the protonic solvent, acetic acid, are explained satisfactorily on the basis of the Brönsted-Lowry concept. Acetic acid is an acidic solvent and a poor proton acceptor; only those substances which are the stronger acids in water, such as perchloric, sulfuric, and hydrochloric acids, may be expected to exhibit marked acidic character in acetic acid. Such indeed has been shown to be the case by Hall and Conant (21), who employed hydrogen ion activity as the criterion of acidity. With regard to basicity in the solvent, it is to be expected that the metal acetates, solely by analogy with the behavior of metal hydroxides in water, should act as bases. Many experimental data have been accumulated to confirm this formal resemblance. In addition, it has been demonstrated that the basic character of substances which are considered weak bases with regard to their behavior towards water is considerably enhanced in acetic acid.

Much of our knowledge concerning acid-base behavior in anhydrous acetic acid comes from the classical investigations of Conant and Hall (21, 22, 23, 24, 25, 26), who showed that glacial acetic acid solutions of organic amines or metal acetates can be titrated electrometrically with solutions of the stronger inorganic acids and the sulfonic acids (21, 22). Potentials reproducible within a few millivolts were obtained with the use of a cell (depicted below) containing as the indicator electrode a platinum foil in an acetic acid solution of chloranil and its reduction product. It is possible to titrate even such weakly basic substances as acetamide, benzamide, and acetanilide.*



By conversion of the experimentally observed potentials to an arbitrarily chosen $(pH)^{\text{HAc}}$ scale, it is possible to determine the relative strengths of various bases. The results of some experiments by Hall and Werner (23) are shown diagrammatically in Figure 14. Since the relative strengths of "strong acids" (HClO_4 , H_2SO_4 ,

* These substances, being weaker bases than water, cannot compete successfully with the latter for the protons of the strong acids and cannot be titrated in aqueous medium.

CCl_3COOH , etc.) differ widely in acetic acid (that is, acetic acid acts as a differentiating solvent toward such substances), perchloric acid, a strong acid in this solvent, is commonly used as the titrant. Exami-

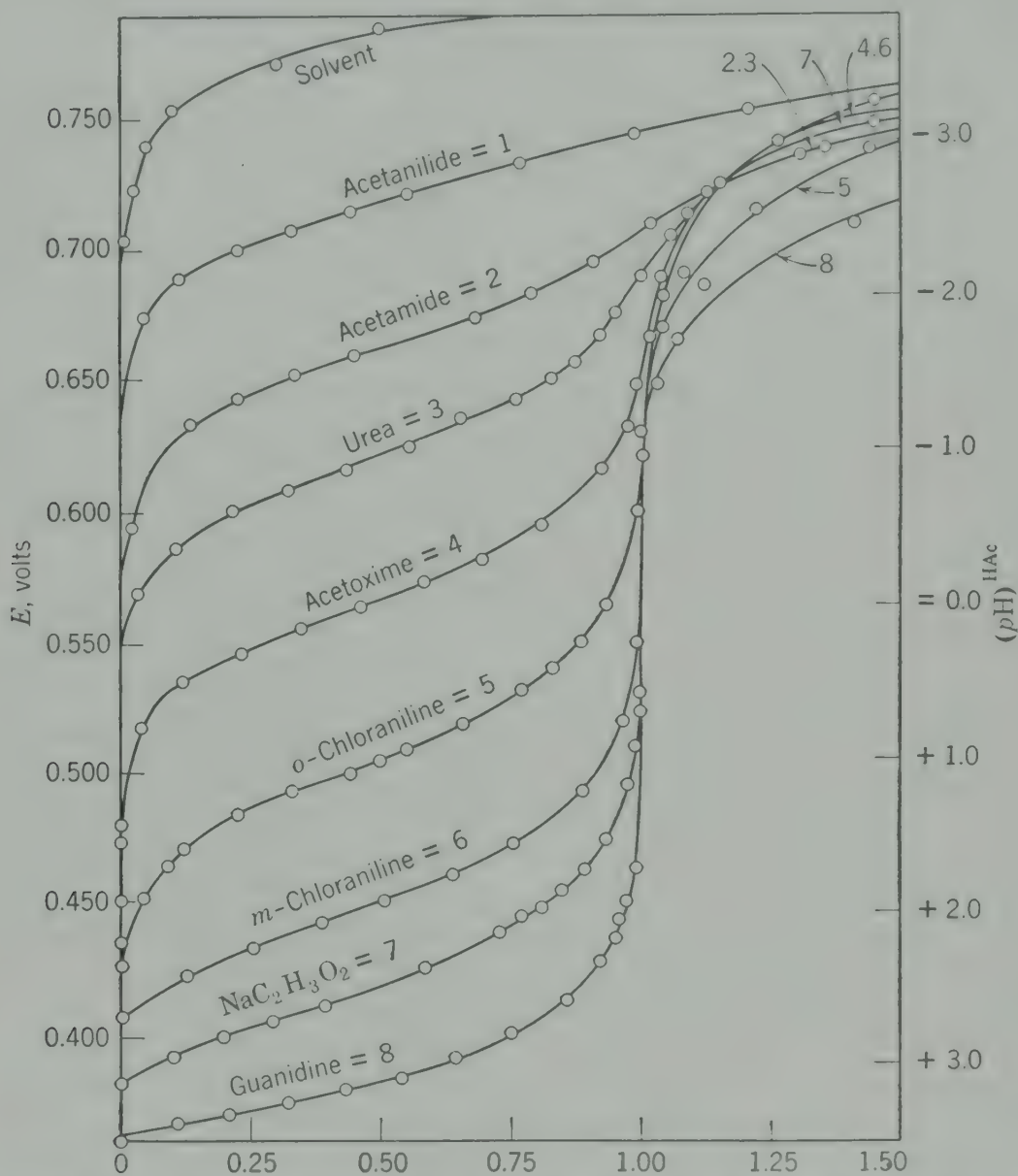


FIGURE 14. Relative strengths of various bases in acetic acid. Titration of 0.05 *N* bases in glacial acetic acid with perchloric acid. Abscissas show fraction of base neutralized.

nation of Figure 14 shows that the curves of strong bases are similar to those for strong bases in water. The weaker bases, however, give curves which are too flat. This anomaly disappears to a large extent when the ionic strength of the solution is maintained at a nearly constant value (25).

It is of importance to point out that even the strongest bases are weak electrolytes in acetic acid (25). This point is clearly illustrated

in Figure 15, where the "apparent" pH values of various dilutions of some bases are plotted against the logarithms of the concentrations. The acidities of the solutions change on dilution in the same manner as those of weak bases in water, namely, as though the electrolyte obeys the dilution law.

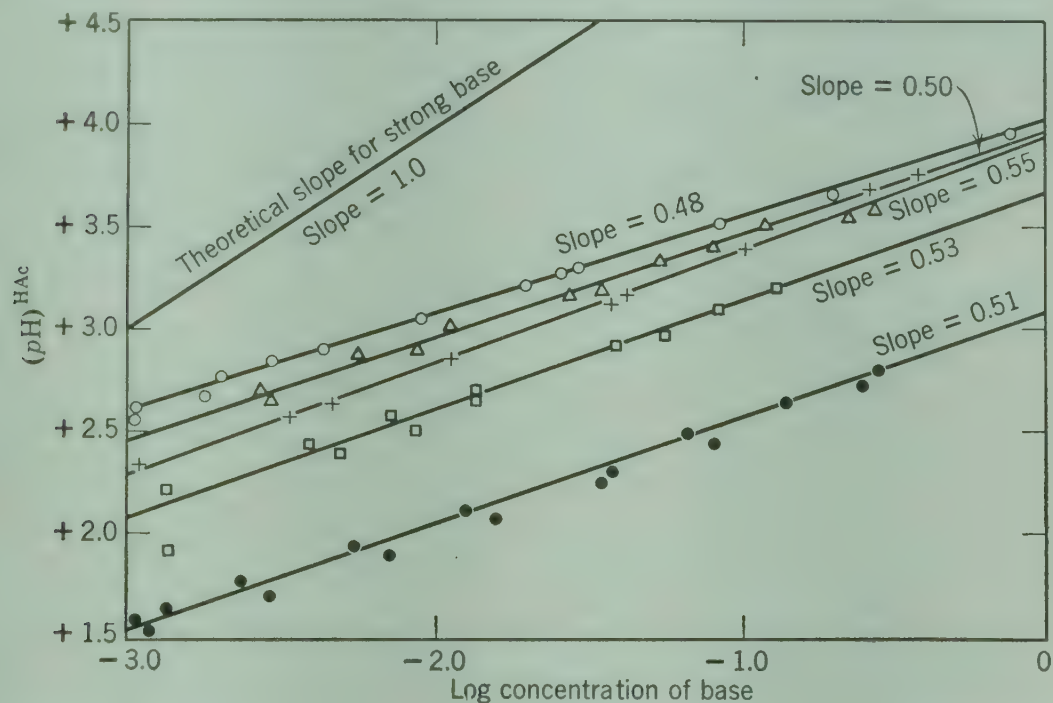
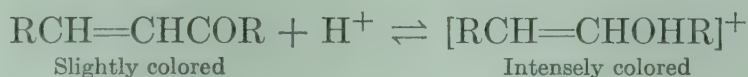
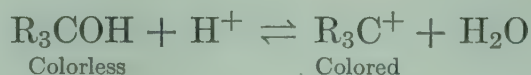


FIGURE 15. $(pH)^{HAc}$ -dilution curves of bases in acetic acid. \circ , diethylamine; $+$, pyridine; \square , sodium acetate; \triangle , guanidine; \bullet , *o*-chloroaniline.

Relative hydrogen activities in acetic acid have also been determined by the use of certain aryl carbinols and unsaturated ketones as indicators (22). The acid-base equilibria involved are formulated below:



The appearance or non-appearance of color when the carbinol is used is a function of the activity both of the hydrogen ion and of the water, whereas whether or not color will appear with the ketone is a function of hydrogen ion activity alone. The carbinols and ketones were tested for the appearance of halochromic color by introducing them into buffer solutions (usually mixtures of sulfuric acid and very weak bases) of graded hydrogen ion activity and with a small and constant water content. The resulting observations were found to be remark-

ably consistent with each other and to agree with those found by the electrometric method previously described.

The dissociation of some acids, bases, and salts in anhydrous acetic acid has been studied by the conductivity method by Kolthoff and Willman (27). The ability of acetic acid to act as a differentiating

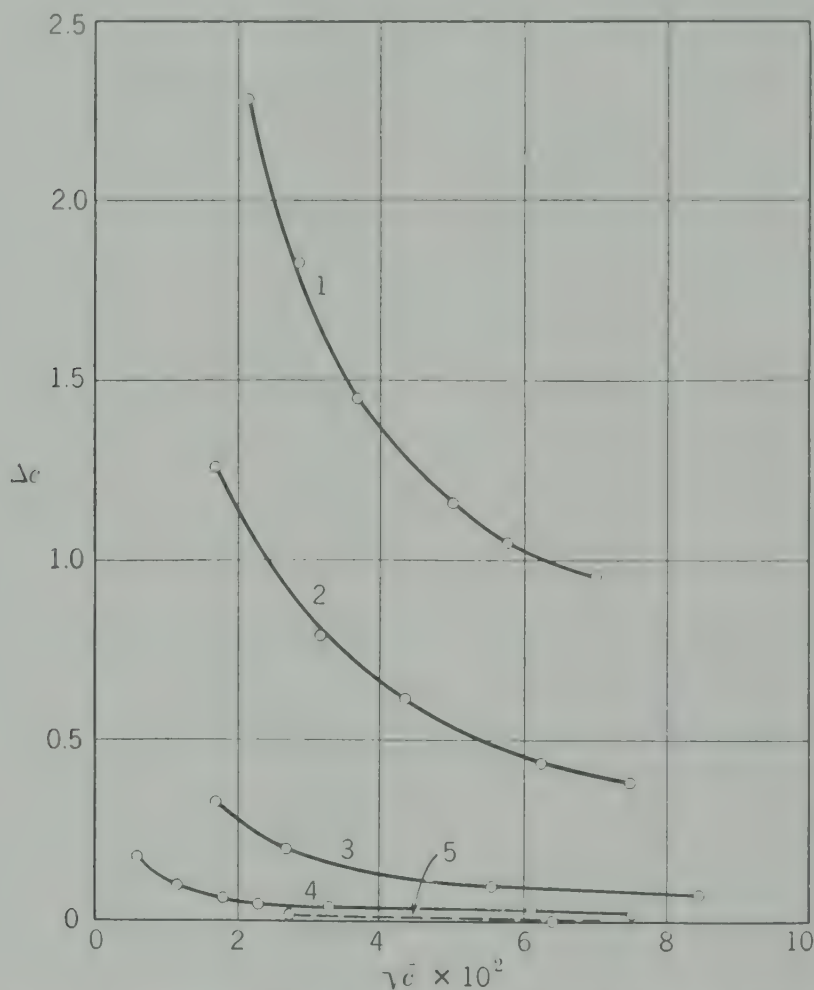


FIGURE 16. Conductances of various inorganic acids in acetic acid.

solvent toward strong acids was confirmed (Figure 16). The relative strengths of a number of acids based on these measurements are given by the following order:



At a concentration of 0.005 molar, the ratio of the conductivities of these acids is 400:160:30:9:1, respectively. However, even the strongest acids (with the exception of perchloric acid) are relatively poor electrolytes in acetic acid. Since acetic acid is a solvent of low dielectric constant, these electrolytes probably exist, even in dilute solution, as ion pairs.

The relative basic strengths of various acetates in acetic acid as determined by measurement of the electrical conductivities are shown in Table 51. These results were verified by the indicator method,

TABLE 51
EQUIVALENT CONDUCTANCES OF ACETATES AT 25°C.

<i>Acetate</i>	<i>Equivalent Conductances, 0.02 Molar Solution</i>
Potassium	0.1217
Ammonium	0.1014
Anilinium	0.0988
Barium	0.0787
Sodium	0.0646
Lithium	0.0587
Strontium	0.0554
Manganese	0.0212
Magnesium	0.0204
Nickel	0.0182
Cadmium	0.0140
Bismuth	0.0103
Lead	0.00857
Urea	0.00185
Diphenylamine	0.00167
Mercuric	0.00096

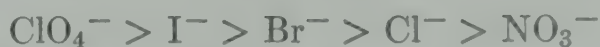
all readings obtained by the use of this method being referred to potassium acetate as a standard. As is the situation with the acids, it is apparent that even the strongest bases are poor electrolytes in acetic acid.

It is interesting to note that ammonium and potassium acetates behave like bases of approximately equal strength. There is other evidence which indicates that ammonium acetate is a strong base in acetic acid. For example, the freezing point curve for ammonium acetate in acetic acid is very similar to that for potassium acetate (11), and the two compounds behave similarly on titration with acids (7). The strongly basic character of ammonium acetate will be mentioned again when amphoteric behavior in acetic acid is considered.

The data of Table 51 indicate that the extent of dissociation of inorganic acetates in acetic acid is a function of the size and charge of the cation. The apparent degree of dissociation decreases with decreasing size and increasing charge of the cation.

It has been demonstrated that salts which undergo no hydrolysis in water may be solvolyzed in acetic acid (27). From studies in which thymolbenzein was used as an acid indicator, it was shown that

the acidity of the potassium salts of some strong inorganic acids decreases in this order:



With 0.002 molar solutions of alkali metal perchlorates the acidity, as measured with the same indicator, decreases in this order:



All the salts studied, with the exception of potassium nitrate, develop an acid reaction in acetic acid. The perchlorates of various dipositive cations and of silver give solutions which are much more acid than those of lithium perchlorate.

REACTIONS IN ANHYDROUS ACETIC ACID

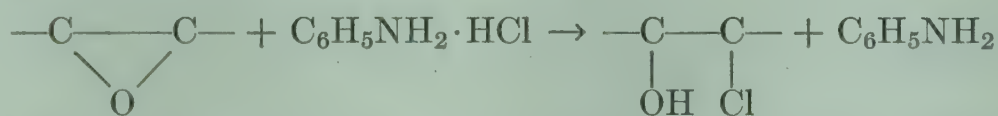
METATHETICAL REACTIONS. The preceding discussion makes it clear that typical acids, bases, and salts are dissociated (although hardly completely) into ions in acetic acid despite its low dielectric constant. Metathetical reactions, therefore, proceed smoothly in this medium (8). For example, treatment of solutions of heavy metal salts with hydrogen sulfide results in the immediate precipitation of the appropriate sulfides. Silver nitrate solution gives precipitates with solutions of halides, cyanides, and thiocyanates. A sulfate or acid sulfate can be precipitated from a solution of almost any soluble metal salt by reaction with anhydrous sulfuric acid. In this manner, sulfates which normally form hydrates can be precipitated in the anhydrous condition. Barium nitrate is sufficiently insoluble to be formed as a precipitate by reaction between solutions of sodium nitrate and barium iodide. The familiar deep red iron(III) thiocyanate complex is formed readily by metathesis in acetic acid.

In addition to the metathetical reactions described above, there are those involving neutralization of metal acetates with acids in acetic acid. Reactions of this type have already been described in connection with acid-base relationships in acetic acid; it was pointed out that their course may be followed by the electrometric titration or by the indicator method. These methods need not be used if there is a pronounced difference in solubility between the reactants and the salt produced. Thus the neutralization of sodium acetate with hydrochloric acid results in the precipitation of sodium chloride; the neutralization of zinc acetate by reaction with the same acid is accompanied by dissolution of the zinc acetate.

REACTIONS DEPENDENT ON ACID-BASE PROPERTIES OF SOLUTES. The enhancement in acetic acid of the basic character of substances ordinarily considered weak bases in water makes it possible to use titration methods for the quantitative estimation of such compounds. Polypeptides (28), amino acids (28, 29, 30), primary, secondary, and tertiary amines (31), and alkylene oxides (31) have been determined quantitatively with considerable success in acetic acid medium, using perchloric acid as titrant. Titrations may be followed either potentiometrically with the use of the chloranil electrode or by the indicator method with such indicators as brilliant cresyl green and blue, crystal violet, α -naphtholbenzein, or benzoyl auramine.*

A number of interesting observations have been made regarding the applicability of this method to the determination of amino acids (30). First of all, the method is capable of a high degree of precision. Second, the difficulty frequently encountered because of the limited solubility of certain amino acids can be overcome by the addition of small amounts of formic acid. Third, it is probable that the method as applied at present gives correct results only with the neutral amino acids; the accuracy is not quite so satisfactory with compounds containing more acidic groups.

The determination of alkylene oxides (31) involves treatment with anilinium chloride in acetic acid and results in the formation of the corresponding chlorohydrin and aniline:



The liberated aniline is then titrated quantitatively with a solution of standard acid in acetic acid.

In addition to the neutral salt effects on solubilities in acetic acid, which have already been discussed, a solubility effect has been observed which may be attributed to the amphoteric character of certain acetates. Our knowledge of amphoteric behavior in acetic acid comes chiefly from the brilliant investigations of Davidson and co-workers (7, 8, 11, 32, 33, 34).

The addition of a small quantity of a solution of sodium acetate in acetic acid to a solution of zinc chloride results in the precipitation of

* Use of standard solutions of perchloric acid in acetic acid for titration of weak bases has also been recommended by a number of investigators in publications which have come to the attention of the authors only recently. Pertinent references include the following: Fritz, *Anal. Chem.*, **22**, 1028 (1950); Seaman and Allen, *Anal. Chem.*, **23**, 592 (1951); Wilson, *J. Soc. Chem. Ind.*, **67**, 237 (1948); Wittmann, *Angew. Chem.*, **A60**, 330 (1948).

zinc acetate. The precipitated zinc acetate may then be dissolved by adding an excess of sodium acetate solution. These reactions are analogous to the precipitation and dissolution of zinc hydroxide upon treatment of an aqueous solution of a zinc salt with sodium hydroxide solution. That the analogy drawn above is not a superficial and formal one is shown by a detailed study of the ternary system $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2$ – $\text{NaC}_2\text{H}_3\text{O}_2$ – $\text{HC}_2\text{H}_3\text{O}_2$ (7, 32). A comparison of Figures 17 and 18

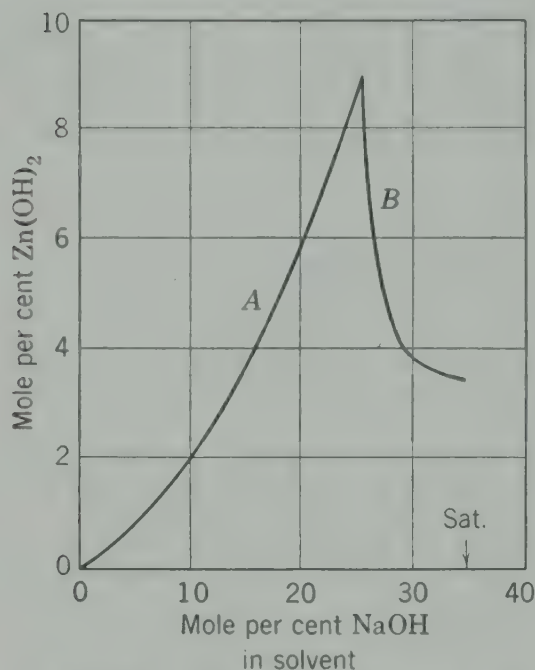


FIGURE 17. Effect of NaOH upon the solubility of $\text{Zn}(\text{OH})_2$ in H_2O at 30°C . A, solid phase $\text{Zn}(\text{OH})_2$; B, solid phase $\text{Zn}(\text{OH})_2 \cdot 2\text{NaOH} \cdot 2\text{H}_2\text{O}$.

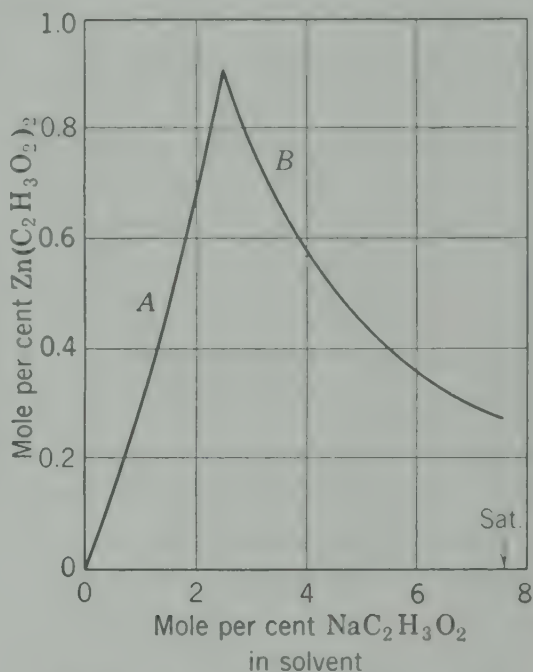


FIGURE 18. Effect of $\text{NaC}_2\text{H}_3\text{O}_2$ upon the solubility of $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2$ in $\text{HC}_2\text{H}_3\text{O}_2$ at 28.5°C .

shows that isotherms for the systems $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2$ – $\text{NaC}_2\text{H}_3\text{O}_2$ – $\text{HC}_2\text{H}_3\text{O}_2$ and $\text{Zn}(\text{OH})_2$ – NaOH – H_2O are strikingly similar. In each system the solubility of the zinc compound increases with increasing concentration of sodium compound until a maximum is attained where a new solid phase appears. Beyond the maximum there is a decrease in the concentration of the zinc compound in the saturated solution with increasing concentration of sodium compound. The solid phases which appear in the two systems at high concentrations of sodium compound are also remarkably similar in composition. They may be formulated as ternary addition compounds of the respective compositions $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{NaC}_2\text{H}_3\text{O}_2 \cdot 4\text{HC}_2\text{H}_3\text{O}_2$ and $\text{Zn}(\text{OH})_2 \cdot 2\text{NaOH} \cdot 2\text{H}_2\text{O}$, or as $\text{Na}_2\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_4 \cdot 4\text{HC}_2\text{H}_3\text{O}_2$ and $\text{Na}_2\text{ZnO}_2 \cdot 4\text{H}_2\text{O}$. The solubility behavior of zinc acetate in acetic acid towards added ammonium acetate is exactly analogous to that just described (34). In

this case the solid solvate has the composition $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{NH}_4\text{C}_2\text{H}_3\text{O}_2 \cdot 6\text{HC}_2\text{H}_3\text{O}_2$. It is of interest to note that no evidence was obtained of a specific effect due to ammonia. Ammonium acetate appears to act solely as a strong base (7, 11, 27).

Additional evidence is available which shows that the dissolution of zinc acetate in alkali metal acetate solutions must be attributed chiefly to chemical effects. Calculation shows that the activity coefficient of zinc acetate in alkali metal acetate solutions falls off much more rapidly with increasing ionic strength than does that of barium acetate in binary solutions (34). Furthermore, from a study of the system $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2\text{--LiC}_2\text{H}_3\text{O}_2\text{--HC}_2\text{H}_3\text{O}_2$, which gives results similar to those obtained for the other systems of zinc acetate with added acetates, the solubility of zinc acetate in a one molal solution of lithium acetate is shown to be 0.29 molal, whereas in one molal lithium nitrate solution its solubility is only 0.08 molal (35). It would certainly appear, therefore, that the solvent effects of these two lithium salts upon zinc acetate are different in character as well as in magnitude.

The solubility of copper(II) acetate in acetic acid is increased in the same manner as that of zinc acetate by the addition of alkali metal or ammonium acetate (33, 34). Solvates of the compositions $2\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{KC}_2\text{H}_3\text{O}_2 \cdot 2\text{HC}_2\text{H}_3\text{O}_2$ and $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{NH}_4\text{C}_2\text{H}_3\text{O}_2 \cdot 4\text{HC}_2\text{H}_3\text{O}_2$ have been isolated. Of interest is the observation that at high temperatures there appears in the ternary system $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2\text{--NH}_4\text{C}_2\text{H}_3\text{O}_2\text{--HC}_2\text{H}_3\text{O}_2$ a violet-blue color which is very similar to that of aqueous solutions of copper(II) hydroxide in ammonia. At low temperatures there appears to be no doubt that the dissolution of copper(II) acetate by added acetate is a manifestation of the amphoteric behavior of the former. At high temperatures it is entirely possible that an ammine complex similar to $\text{Cu}(\text{NH}_3)_4^{++}$ is formed and is responsible for the violet-blue color, since there is evidence that ammonium acetate in warm solutions of acetic acid undergoes dissociation according to the following equilibrium (36):



The system $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2\text{--NaC}_2\text{H}_3\text{O}_2\text{--HC}_2\text{H}_3\text{O}_2$ has also been investigated (37). Although the solubility of lead acetate is increased as more and more sodium acetate is added, no addition compound similar to those isolated in the other ternary systems was obtained. In contrast to the behavior of lead(II) acetate, the solubility of the acetate of tetrapositive lead *decreases* with increasing concentration of added sodium acetate (38). No evidence of amphoterism is ob-

tained. Indeed, the solubility behavior of lead(IV) acetate may be considered to be an example of the "salting out" of a typical non-electrolyte. That lead(IV) acetate is definitely non-electrolytic in character is indicated by the extremely low conductivity of its solutions and by its inability to take part in rapid metathetical reactions in this solvent.

ELECTROCHEMICAL OXIDATIONS IN ACETIC ACID. The anodic oxidation of certain metals in an electrolyte of an alkali metal acetate dissolved in anhydrous acetic acid has served as a convenient method for the preparation of the corresponding anhydrous acetates (39, 40). This method is particularly useful as a source of the anhydrous acetates of some of the less active metals which, with the exception of lead(II) acetate, are relatively insoluble in acetic acid. Thus the acetates of mercury (I), zinc, iron(III), and the monosolvate of copper(II) acetate have been made in high yield and a relatively high degree of purity.

The oxidation of cobalt(II) and nickel(II) acetates in acetic acid at an inert anode has been studied and is presumed to result in the formation of the acetates of the tripositive metals. Data on this subject (41, 42) are, however, of a conflicting nature, and the matter is worthy of further investigation.

The anodic behavior of the elements of the aluminum family in anhydrous acetic acid containing sodium or ammonium acetate as elec-

TABLE 52

COMPARISON OF THE ANODIC BEHAVIOR OF THE ELEMENTS OF THE ALUMINUM FAMILY IN WATER AND IN ACETIC ACID

<i>Element</i>	<i>Water *</i>		<i>Acetic Acid †</i>	
	<i>Initial Oxidation No.‡</i>	<i>Final Oxidation No.§</i>	<i>Initial Oxidation No.‡</i>	<i>Final Oxidation No.§</i>
Tl(NaNO ₃ electrolyte)	1	1	1	1
In	3	3	2.1-2.9	0 and 3 (disproportionation)
Ga	3	3	1.1-2.0	1.5-2.8
Al	1.9-2.6	3	1.8-2.8	3

* Electrolyte: NaCl.

† Electrolyte: NaC₂H₃O₂.

‡ Calculated from loss in weight of anode on basis of Faraday's law.

§ Determined by titration of electrolyte solution with standard iodine solution on completion of electrolysis.

trolyte has been the subject of intensive investigation (43, 44). Electrolyses were carried out in a carbon dioxide atmosphere, usually with a fritted glass disk separating anolyte and catholyte. The results of these studies demonstrate that aluminum, gallium, and indium go into solution in oxidation states lower than +3. The comparative anodic behavior of these elements in water and in acetic acid as solvents (44) is summarized in Table 52.

The results of electrolytic experiments in acetic acid show the necessity for postulating that at least some of the aluminum and gallium enters solution as unipositive ions. It is apparent that the oxidation number of the dissolved metals in the electrolyte solution following electrolysis experiments in which aluminum and gallium anodes were employed is considerably greater than the number calculated from loss in weight of the anode. This is not surprising in view of the formation in solution of a powerful reducing agent which reacts with the solvent to liberate hydrogen, presumably as a result of the reaction



The experimental conditions favoring the formation of unipositive aluminum are listed below:

Electrolyte: 3 to 6 mole per cent of $NaC_2H_3O_2$ in $HC_2H_3O_2$.

Current density: ca. 0.007 amp. per cm^2 .

Temperature: 20°C.

Cathode: platinum.

ELECTROCHEMICAL REDUCTIONS IN ACETIC ACID. An attempt to utilize acetic acid as a medium for the plating of metals has met with indifferent success. The discharge of antimony, arsenic, and bismuth from solutions of their chlorides in glacial acetic acid has been reported, the structures of the deposits being determined by means of x-ray diffraction analysis (45). It was found that low temperatures favor the formation of the amorphous form of antimony, whereas the crystalline form is obtained at higher temperatures. An amorphous form of arsenic, as a black, lustrous, metallic plate is obtained from solutions of the trichloride; bismuth is deposited in the crystalline form.

Polarographic studies in acetic acid have yielded interesting information. MacGillavry (46) had originally found that dissolved oxygen has no effect on polarographic curves in acetic acid, but the work of Bachman and Astle (47) appears to refute this statement. These investigators have demonstrated that an oxygen maximum does occur in anhydrous acetic acid and that the first inflection in the curves obtained by MacGillavry must be attributed to the presence

of oxygen, since it disappears when the solution is degassed. In other respects the two investigations are in agreement. The current-voltage curves at the dropping mercury cathode are straight lines for low concentrations of such electrolytes as lithium chloride and sodium acetate; inflections in the curves are obtained only in concentrated solutions.

Bachman and Astle demonstrated that certain metallic ions behave in a normal fashion in acetic acid at the dropping mercury electrode, whereas others do not. Among ions studied were Pb^{+2} , Cd^{+2} , Zn^{+2} , Co^{+2} , Cr^{+3} , Ni^{+2} , Cu^{+2} , Fe^{+3} , and Hg^{+2} ; acetates were employed as solutes, except for iron and bismuth, where the chlorides were used. The first six ions give characteristic S-shaped curves in which the current rise occurs at a potential somewhat higher than it does in water. The current rise is, however, proportional to the concentration of the reducible ion. The current-voltage curves are readily obscured by oxygen, and substances such as gelatin, methylcellulose, and various dyes which are used to eliminate oxygen maxima in aqueous medium are without effect in acetic acid.

Comparisons between wave heights and half-wave reduction potentials in water and acetic acid for those ions which give normal reduction curves are presented in Table 53. The smaller wave heights ob-

TABLE 53

WAVE HEIGHTS AND HALF-WAVE POTENTIALS IN ACETIC ACID

(Concentration of ion is 0.001 *M*. Supporting electrolyte is 0.25 *M* $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ in each case.)

Ion	Wave Heights in Microamperes		Half-Wave Potentials vs. Saturated Calomel Electrode	
	H_2O	$\text{HC}_2\text{H}_3\text{O}_2$	H_2O	$\text{HC}_2\text{H}_3\text{O}_2$ *
Pb^{+2}	3.92	2.24	-0.48 volt	-0.70 volt
Cd^{+2}	3.52	2.24	-0.59	-0.83
Zn^{+2}	3.52	2.22	-1.05	-1.25
Co^{+2}	3.44	2.16	-1.25	-1.35
Ni^{+2}	3.32	2.22	-1.05	-1.15

* Measured against the chloranil electrode and converted to potentials corresponding to the saturated calomel electrode.

tained in acetic acid are to be expected, since the diffusion coefficients for reducible ions are in general smaller in this medium than in water. Data could not be obtained for Cr^{+3} because of the interference of the H^{+} ion wave which appears at about -1.7 volts in degassed solutions. This early appearance of the H^{+} ion wave is a marked disadvantage in the application of the polarographic method to acetic acid

solutions. Substances (both inorganic and organic) with half-wave potentials between -0.3 and -1.4 volts can be determined normally in acetic acid. Other substances (with values more positive than -0.3 volt) give discontinuous curves or (with values more negative than -1.4 volts) are subject to interference by the H^+ ion curve and cannot be determined polarographically in acetic acid.

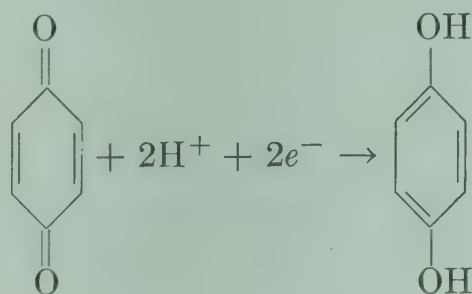
Conant and Chow (48) have determined the reduction potentials of some quinonoid compounds in glacial acetic acid by the potentiometric method. The hydrogen ion activity, as determined by measurement with the chloranil electrode against the saturated calomel electrode, was kept constant in each experiment by means of suitable buffers. The ionic strength was also maintained at a constant value, 0.2, in all buffers. The measured potential, E_h , was defined in glacial acetic acid solutions with reference to a hypothetical hydrogen electrode (1 atm.) functioning in a buffered solution of ionic strength 0.2 and $(pH)^{HAc} = 0$. The potentials were actually measured against a saturated calomel electrode through a lithium chloride bridge, and the values obtained were referred to the hypothetical hydrogen electrode described above. The two methods used for varying the ratio of oxidant and reductant, namely, the method of mixtures and the titration of oxidant with chromium(II) acetate, gave results which were in excellent agreement. The values for the reduction potentials of the compounds subjected to study are listed in Table 54. The recorded

TABLE 54

REDUCTION POTENTIALS OF SOME QUINONOID COMPOUNDS

<i>Compound</i>	E_h^0 at $(pH)^{HAc} = 0$
Chloranil	+0.675 volt
Benzoquinone	+0.650
Indothymol	+0.600
Indo- <i>o</i> -cresol	+0.575
<i>o</i> -Cresol-indophenol	+0.575

potentials are for the type reaction illustrated below for the specific case of benzoquinone:



A plot of the relationship between $(pH)^{HAc}$ and E_h^0 (Figure 19) shows that the results lie on a straight line with theoretical slope

$$\left(\frac{\Delta E_h^0}{\Delta (pH)^{HAc}} = -0.060 \right)$$

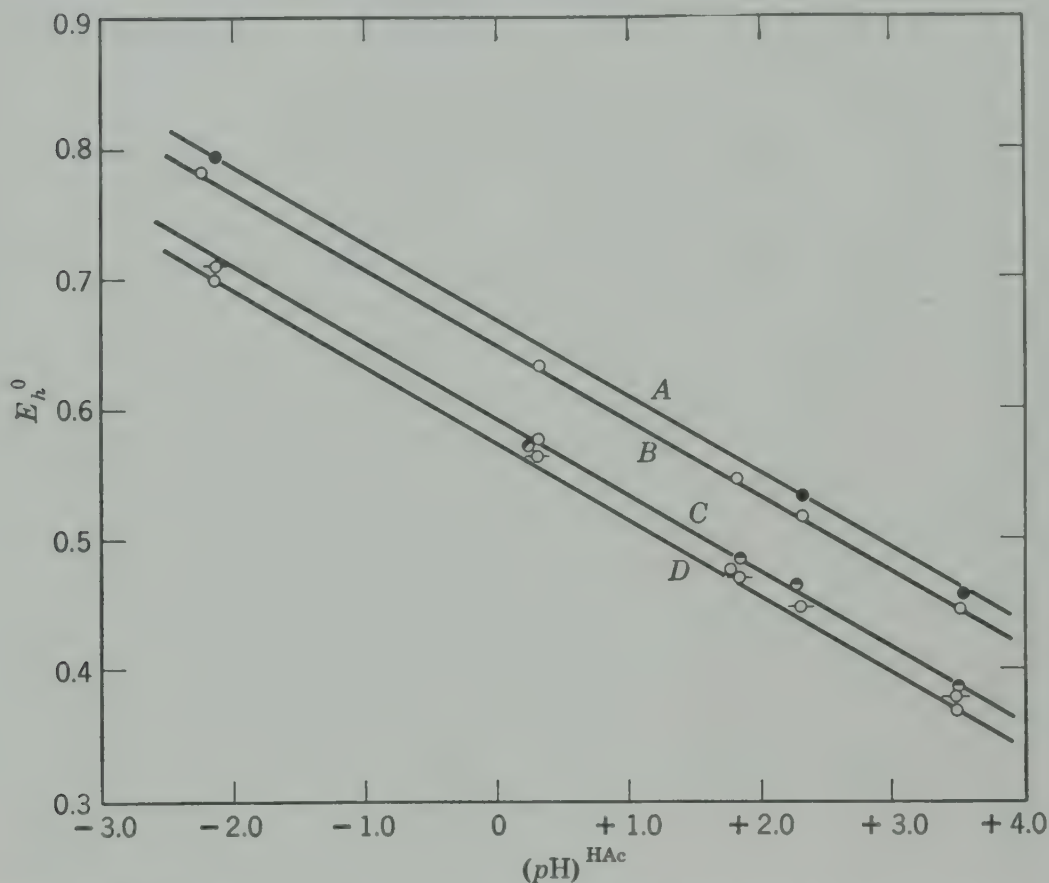
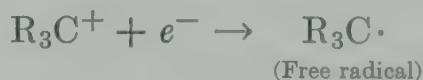


FIGURE 19. The relationship between pH and E_h^0 in acetic acid. The lines were drawn with the theoretical slope: *A*, chloranil; *B*, benzoquinone; *C* (\bullet), indothymol; *D* (\circ), indo-*o*-cresol; (\circ), *o*-cresol-indophenol.

Conant and Chow (49) also measured the reduction potentials of some halochromic ions of the triphenylmethyl type in a similar manner. The following electrode reaction was studied:



The results of these measurements are given in Table 55. Here, as with the quinonoid substances, the potentials vary with changes in acidity of the buffer in accord with theory.

ORGANIC REACTIONS IN ACETIC ACID. Bailey and coworkers (50, 51, 52, 53) have described a series of reactions involving the addition.

TABLE 55

POTENTIALS FOR REACTION: $R_3C^+ + \frac{1}{2}H_2 \rightleftharpoons R_3C\cdot + H^+$ [at $(pH)^{HAc} = 0$]

<i>Halochromic Ion</i>	E_h^0 at $(pH)^{HAc} = 0$
Triphenylmethyl [$(C_6H_5)_3C^+$]	+0.290 volt
Phenylxanthyl [$C_6H_5C^+-(C_6H_4)_2O$]	+0.095
Benzylxanthyl [$C_6H_5CH_2C^+-(C_6H_4)_2O$]	-0.062

in glacial acetic acid, of cyanic acid to compounds containing the —NH— group. With a number of weak nitrogen bases, difficultly soluble in water, carbamido (ureido) derivatives are formed readily in acetic acid by the addition of potassium cyanate. Hydrocyanic acid adds quantitatively to benzalazine to give benzalhydrazinophenyl-acetonitrile (53). By heating primary amines with urea in acetic acid as solvent, practically quantitative yields of symmetrically substituted ureas may be obtained (54). Such a reaction does not take place, however, if the amino group is too faintly basic (for example, the amino groups in glycine or anthranilic acid).

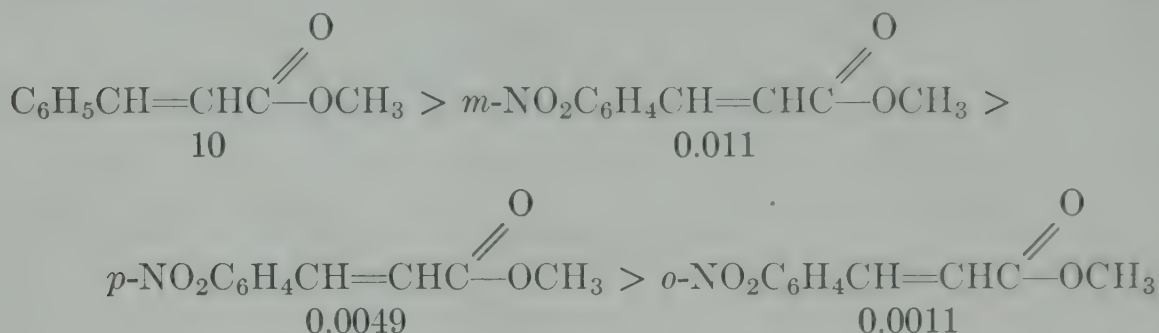
The addition, in acetic acid medium, of chlorine and bromine to various α,β -unsaturated aldehydes has been investigated in order to determine the mechanism of reaction (55). The acid-catalyzed addition of these halogens to cinnamaldehyde, crotonaldehyde, and acrylaldehyde reveals reaction kinetics and relative velocities which indicate a nucleophilic mechanism. The relative catalytic effects of the acids used in the reaction between cinnamaldehyde and bromine are given by the order:



The addition of water to the acetic acid solution of the aldehyde reduces the nucleophilic rate of halogen addition, and with sufficient water the electrophilic reaction is established. The effect of the water is presumably due to its successful competition with the aldehyde for the proton of the acid added as catalyst. As would be expected, the addition of sodium acetate, a strong base, eliminates the acid-catalyzed reaction also.

It has been demonstrated that in acetic acid, chlorine, in the absence of acid catalysts, adds to α,β -unsaturated esters and acids by an electrophilic mechanism (56). The relative bimolecular rates of addition

to methyl cinnamate and its nitro derivatives at 24°C. are summarized below:



The data emphasize the expected reduction in rate of addition due to the presence of the electron-attracting nitro group on the benzene nucleus. This effect is, as would be predicted, smaller when the nitro group is in the meta than in the para position. In the former position the inductive effect alone is operative, whereas in the latter position there is also an important resonance effect.

The mechanism of HBr_3 (that is, $\text{Br}_2 + \text{HBr}$) addition to α,β -unsaturated acids is apparently dependent upon the electron density at the ethylenic carbon atoms (56). For example, in β,β -dimethylacrylic

acid, $(\text{CH}_3)_2\text{C}=\text{CH}-\text{C}(=\text{O})\text{OH}$, where the methyl groups serve to increase the electron density at the double bond, the addition mechanism is an electrophilic one. On the other hand, the addition proceeds by a nucleophilic route in acrylic acid where the electron availability is less. For compounds of the acrylic acid type (that is, with low electron density at the double bond), the addition of bromine is slow, unless catalyzed by the presence of hydrogen bromide.

The acetylation of β -naphthol with acetic anhydride in acetic acid as solvent offers a particularly noteworthy example of acidic and basic catalysis in a non-aqueous medium (57). Figure 20 shows the relationship between the logarithm of the specific reaction rate for this reaction and the electrometrically determined $(\text{pH})^{\text{HAc}}$. Acid solutions were obtained by the use of perchloric, sulfuric, phosphoric, and naphthalenesulfonic acids or by solutions of sulfuric acid buffered with such weak bases as acetamide and benzamide. The acid portion of the curve indicates a specific catalytic effect due to the solvated proton. The rate goes through a minimum at approximately $(\text{pH})^{\text{HAc}} = 0$, and then increases with either added acetate ion or pyridine. The latter observation indicates that the basic catalysis is of a general nature. It is evident from Figure 20 that it is possible

to regulate quite closely the rate of the acetylation reaction by the proper choice of buffer solution.

Acetic acid has been used successfully as a medium for the halomethylation of aromatic derivatives (58, 59, 60, 61). It has been reported (58) that 1-chloromethyl naphthalene may be prepared in 95% yield in acetic acid by long heating of trioxymethylene, dry hydrogen chloride, and naphthalene. This yield, however, has not been dupli-

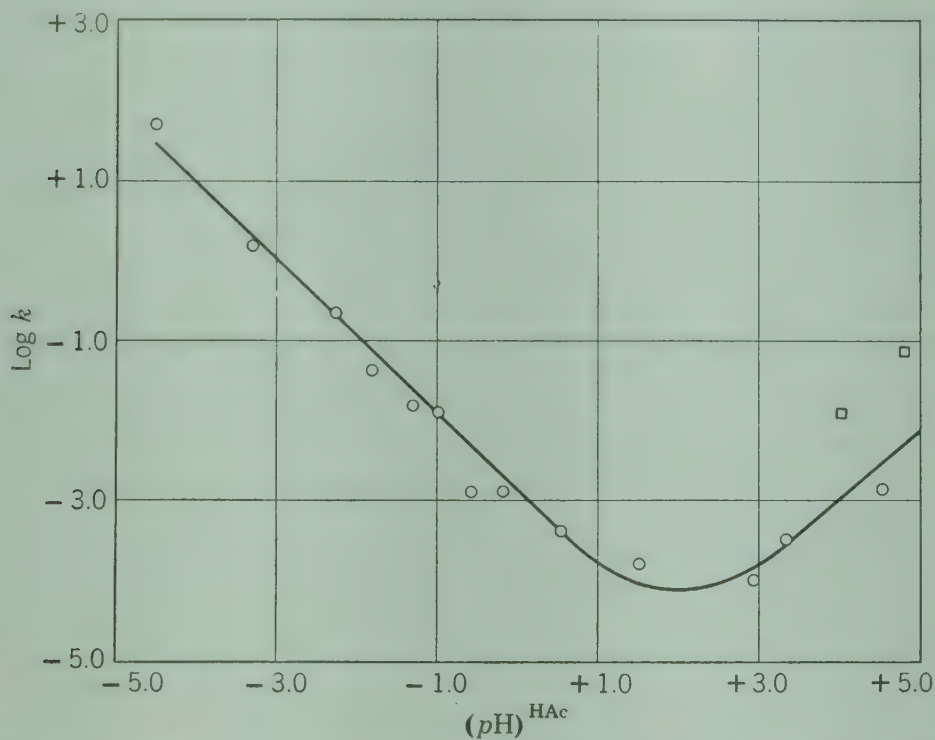


FIGURE 20. The rate of acetylation of β -naphthol in acetic acid solutions. \square , pyridine.

cated by other investigators (60, 61). Other halomethyl derivatives of naphthalene and substituted naphthalenes have also been prepared similarly in excellent yield (58). Toluene may also be caused to undergo successful halomethylation under more stringent conditions (59). With halo and nitro derivatives of benzene it is necessary to add condensing agents, such as zinc chloride or acetic anhydride, in order to obtain a good return of the desired product.

The mixed chlorination of ethylene, involving addition of the halogen and the acetoxy group, has been effected in acetic acid medium (62). β -Chloroethylacetate may be prepared in 40% yield by reaction between chlorine and the olefin in this solvent; it is necessary to keep the halogen concentration low to avoid large yields of the dichloride. A similar reaction results when ethylene is chlorinated in either acetic anhydride or methyl acetate. The addition of bromine

to butadiene in glacial acetic acid containing dissolved sodium acetate gives approximately 70% of the 1,4-dibromide (63). The monomer-curation of benzene may be carried out, with excellent results, by means of mercury(II) acetate in glacial acetic acid as solvent at 110°C. (64).

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64. Kobe and Lueth, *Ind. Eng. Chem.*, **34**, 309 (1942).

SULFURIC ACID

Within the last ten years sulfuric acid has assumed a position of some importance as a medium for certain types of organic reactions, particularly those involving very weak bases as reactants. There is every indication that its utility as a solvent for these reactions will be increased considerably in the future. By contrast, comparatively little has been done with this solvent in the field of inorganic chemistry. It is to be hoped that the survey of sulfuric acid chemistry which follows may serve as a stimulus to the inorganic chemist and that this potentially valuable solvent for inorganic reactions will no longer be neglected.

Since sulfuric acid of excellent quality is available in concentrations both above and below that corresponding to 100% H_2SO_4 , the preparation of the latter material may be accomplished readily (1, 2). Essentially, the method of preparation consists of mixing concentrated and fuming sulfuric acids in the appropriate proportions. A freezing point of approximately 10.5°C . for the mixture indicates that a composition corresponding to the 100% acid has been attained. Actually, for cryoscopic work, a sufficient excess of water is added to give an acid which freezes at about 10.3°C . The reason for this is discussed later.

The physical properties of the 100% acid are generally favorable from an investigative viewpoint. It is liquid over the wide range from 10.5° to approximately 322°C . Although no exact value for the dielectric constant is available, there is no doubt that it is greater than that of water. Walden (3) has stated that the dielectric constant of commercial sulfuric acid (sp. gr. 1.85) is greater than 84. As a result of the high dielectric constant, interionic forces are extremely small in absolute sulfuric acid. The solvent exhibits a high degree of self-ionization, as is evident from the generally accepted value of $1 \times 10^{-2} \text{ ohm}^{-1}$ for its specific conductance (4). The high viscosity of sulfuric acid, 267 millipoises at 20° (5) as compared to a corresponding value for water of 10.1 millipoises, is its major adverse

property. As a result of the high viscosity substances dissolve very slowly, except at inconveniently high temperatures. Moreover, crystallization from solutions in this solvent is also likely to be slow; extreme supercooling is experienced frequently. In addition, it is difficult to remove adhering solvent from separated crystals (6).

The strongly acid nature of absolute sulfuric acid makes it an excellent solvent for the study of weak bases (that is, substances which are weakly basic in water). Perchloric (7) and pyrosulfuric (8) acids are the only substances which have been reported to possess acidic character in absolute sulfuric acid.

SOLVENT PROPERTIES

SOLUBILITIES AND REACTIONS OF INORGANIC COMPOUNDS. Davidson (6) and Kendall and co-workers (9, 10) have determined the solubilities of a large number of inorganic compounds in 100% sulfuric acid.

TABLE 56

QUALITATIVE SOLUBILITIES OF SALTS IN ABSOLUTE SULFURIC ACID

Readily Soluble (No Visible Reaction at Room Temperature)

Li_2SO_4	K_2SO_4	Ag_2SO_4
NaNO_3	$\text{K}_4[\text{Fe}(\text{CN})_6]$	CaF_2
Na_2HAsO_4	$\text{K}_3[\text{Fe}(\text{CN})_6]$	$\text{Ca}_3(\text{PO}_4)_2$
KNO_3	AgNO_3	BaSO_4
KSCN		

Difficultly Soluble

CaCO_3 (CO_2 evolved slowly)
Hg_2SO_4
MgSO_4
ZnSO_4
FeSO_4

Insoluble

AgCl
CuBr_2 *
CuSO_4
HgSO_4
PbSO_4
NiSO_4
AlCl_3
AlPO_4
$\text{Al}_2(\text{SO}_4)_3$
$\text{Fe}_2(\text{SO}_4)_3$

Solvolyzed with Product Soluble

NaCl (HCl evolved, even at $0^\circ\text{C}.$)
NaBr (HBr evolved)
KCl (HCl evolved, even at $0^\circ\text{C}.$)
KBr (orange solution formed)
KI (I_2 formed, even at $0^\circ\text{C}.$)
CaCl_2 (HCl slowly evolved)

Solvolyzed with Product Insoluble

Na_2SiO_3
$\text{Al}(\text{NO}_3)_3$
$\text{Fe}(\text{NO}_3)_3$
FeCl_3
$\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$

* Dissolves on heating to yield elementary bromine.

Qualitative solubility data obtained from the reports of these investigators are given in Table 56.

The following pertinent observations may be made regarding the solubility of salts in absolute sulfuric acid (6). Salts are extensively solvolyzed in sulfuric acid. This is not surprising in view of the high degree of ionization of both solvent and solute. Salts of metals whose sulfates are insoluble are either insoluble (for example, AlPO_4) or else are extensively solvolyzed [for example, $\text{Fe}(\text{NO}_3)_3$] to the insoluble sulfates. Salts of acids which in the free state are insoluble in sulfuric acid are either themselves insoluble (for example, AgCl , CuBr_2), or else are solvolyzed (NaCl) to yield the insoluble acid. Salts of metals whose sulfates are soluble and of acids which are soluble are generally soluble in anhydrous sulfuric acid. Attempts to recover unchanged two readily soluble, highly ionized salts, $\text{K}_4[\text{Fe}(\text{CN})_6]$ and $\text{Ca}_3(\text{PO}_4)_2$, from solution in sulfuric acid were unsuccessful; instead, the respective products of solvolysis, $\text{H}_4\text{Fe}(\text{CN})_6 \cdot 6\text{H}_2\text{SO}_4$ and $\text{CaSO}_4 \cdot \text{H}_2\text{SO}_4$, were obtained.

Kendall and collaborators (9, 10) carried out a systematic study of the solubility of metal sulfates in anhydrous sulfuric acid by the freezing point method. It was demonstrated that the order of solubility of the various metal sulfates parallels almost exactly the order of solubility of the corresponding hydroxides in water. Moreover, it was

TABLE 57

SOLUBILITY OF METAL SULFATES IN SULFURIC ACID AT 25°C.

<i>Metal</i>	<i>Solubility, Mole %</i>	<i>Solid Phase</i>
Li	14.28	$\text{Li}_2\text{SO}_4 \cdot 2\text{H}_2\text{SO}_4$
K	9.24	$\text{K}_2\text{SO}_4 \cdot 3\text{H}_2\text{SO}_4$
Ba	8.85	$\text{BaSO}_4 \cdot 3\text{H}_2\text{SO}_4$
Na	5.28	$2\text{Na}_2\text{SO}_4 \cdot 9\text{H}_2\text{SO}_4$
Ca	5.16	$\text{CaSO}_4 \cdot 3\text{H}_2\text{SO}_4$
Mg	0.18	$\text{MgSO}_4 \cdot 3\text{H}_2\text{SO}_4$
Al	<0.01	$\text{Al}_2(\text{SO}_4)_3$
Zn	0.17	$\text{ZnSO}_4 \cdot x\text{H}_2\text{SO}_4$
Fe(II)	0.17	$\text{FeSO}_4 \cdot x\text{H}_2\text{SO}_4$
Ni	very small	NiSO_4
Pb	small	PbSO_4
Fe(III)	<0.01	$\text{Fe}_2(\text{SO}_4)_3$
Cu	0.08	CuSO_4
Hg(I)	0.78	$\text{Hg}_2\text{SO}_4 \cdot \text{H}_2\text{SO}_4$
Ag	9.11	$\text{Ag}_2\text{SO}_4 \cdot 2\text{H}_2\text{SO}_4$
Hg(II)	0.02	HgSO_4

TABLE 58

SOLVATES ISOLATED FROM METAL SULFATE-SULFURIC ACID SYSTEMS

<i>Compound</i>	<i>Melting Point, °C.</i>	<i>Remarks</i>
$K_2SO_4 \cdot 3H_2SO_4$	91.5°	Stable at m.p.
$K_2SO_4 \cdot H_2SO_4$	218.6°	Stable at m.p.; exists in three modifications with transition points at 182° and 202°C.
$(NH_4)_2SO_4 \cdot 3H_2SO_4$	48.0°	Stable at m.p.
$(NH_4)_2SO_4 \cdot H_2SO_4$	146.9°	Stable at m.p.
$2Na_2SO_4 \cdot 9H_2SO_4$	60°	Transition points to the two modifications of $Na_2SO_4 \cdot 2H_2SO_4$ occurring at 57° and 58°C.
	(extrapolation)	
$Na_2SO_4 \cdot 2H_2SO_4$		Two modifications, both unstable at their m.p.; transition to $Na_2SO_4 \cdot H_2SO_4$ occurring at 95° and 109°C.
$Na_2SO_4 \cdot H_2SO_4$	186°	Stable at m.p.
$Li_2SO_4 \cdot 2H_2SO_4$		Unstable at m.p.; transition to $Li_2SO_4 \cdot H_2SO_4$ occurring at 50°C.
$Li_2SO_4 \cdot H_2SO_4$	170.5°	
	(extrapolation)	
$BaSO_4 \cdot 3H_2SO_4$		Unstable at m.p.
$CaSO_4 \cdot 3H_2SO_4$		Unstable at m.p. Exists in two modifications.
$MgSO_4 \cdot 3H_2SO_4$		Unstable at m.p.
$ZnSO_4 \cdot xH_2SO_4$		Composition undetermined.
$FeSO_4 \cdot xH_2SO_4$		Composition undetermined.
$Hg_2SO_4 \cdot H_2SO_4$		Unstable at m.p.
$Ag_2SO_4 \cdot 2H_2SO_4$		Unstable at m.p.
$Ag_2SO_4 \cdot H_2SO_4$		Unstable at m.p. Two crystalline modifications with a transition point at 66°C.

also shown that solvate formation * and solubility proceed hand in hand. The data obtained by these investigators are summarized in Tables 57 and 58.

Davidson (6) studied the effect of added sodium sulfate on the solubilities of aluminum, zinc, and lead sulfates in anhydrous sulfuric acid, in order to determine whether these substances are amphoteric in this medium. In no case was solubility increased by the addition of sodium sulfate. Actually, there was observed a decrease in solubility, which may be attributed to the common ion effect.

Metathetical reactions can also take place in absolute sulfuric acid, but, because of the high viscosity of the solvent, metathesis is not

* The solvates, particularly those of the 1:1 type, may alternatively be formulated as acid sulfates. For example, $Na_2SO_4 \cdot H_2SO_4$ may be written as $NaHSO_4$.

always instantaneous. Reaction between sodium chloride and silver nitrate solutions results in the immediate precipitation of silver chloride. In this connection it is of interest to note that silver chloride is formed even after the sodium chloride solution has been boiled for several minutes before the silver nitrate is added. This indicates that solvolysis of sodium chloride is far from complete even at the boiling point of sulfuric acid, despite the low solubility of hydrogen chloride at this temperature. Silver bromide is precipitated when solutions of potassium bromide and silver nitrate are mixed. The addition of sodium chloride solution to mercury(I) sulfate gives a heavy white precipitate of mercury(I) chloride. A saturated solution of copper(II) sulfate slowly yields a yellow gelatinous precipitate of the chloride upon treatment with sodium chloride solution. The bromide is produced by a similar reaction. Although hydrogen sulfide is rapidly oxidized by anhydrous sulfuric acid it is possible to precipitate silver sulfide by passage of the gas into a solution of silver nitrate. The precipitate gradually reacts with the solvent to form sulfur dioxide and free sulfur. A similar reaction does not take place when the gas is passed into mercury(I) sulfate or lead sulfate solution; in these cases, only sulfur is precipitated.

Because of the highly acid nature of the medium relatively few substances are capable of exhibiting acidic properties in absolute sulfuric acid. Neutralization reactions in which sulfuric acid acts merely as the solvent are, therefore, of little importance. Usanovich (7) has reported that perchloric acid may be used in this medium as an acid titrant for the bases sodium acid sulfate and water. The titrations were carried out conductometrically and the curves obtained showed definite, but not sharp, breaks at the neutralization points. This type of behavior is to be expected in a solvent so highly self-ionized as sulfuric acid. It is conceivable, however, that non-protonic Lewis acids, such as sulfur trioxide, boron trifluoride and similar compounds, will be found to act as acids in 100% sulfuric acid.

SOME ELECTROCHEMICAL PROPERTIES OF INORGANIC ELECTROLYTES IN SULFURIC ACID. A considerable quantity of data concerning the electrolytic nature of solutions of inorganic and organic substances in sulfuric acid has been collected from both freezing point data and conductivity measurements. The experimental results of the early investigators in this field * showed that absolute sulfuric acid has great

* The following are pertinent references dealing with the early work on the cryoscopic behavior and conductivities of sulfuric acid solutions: Walden, *Z. anorg. Chem.*, **29**, 371 (1902). Beckmann, *Z. physik. Chem.*, **53**, 129 (1905). Hantzsch, *Z. physik. Chem.*, **61**, 257 (1908); **62**, 626 (1908); **65**, 41 (1909); **68**, 204

ionizing power, but not much of a quantitative nature could be determined concerning the degree of dissociation of solutes in this medium because of the great number of unknown factors involved. In fact, many of the data are of a contradictory nature. The reason for the contradictory observations has been explained in large measure by the excellent work of Hammett and Deyrup (11), who have placed the determination of cryoscopic behavior and conductivities in sulfuric acid on a firm theoretical basis.

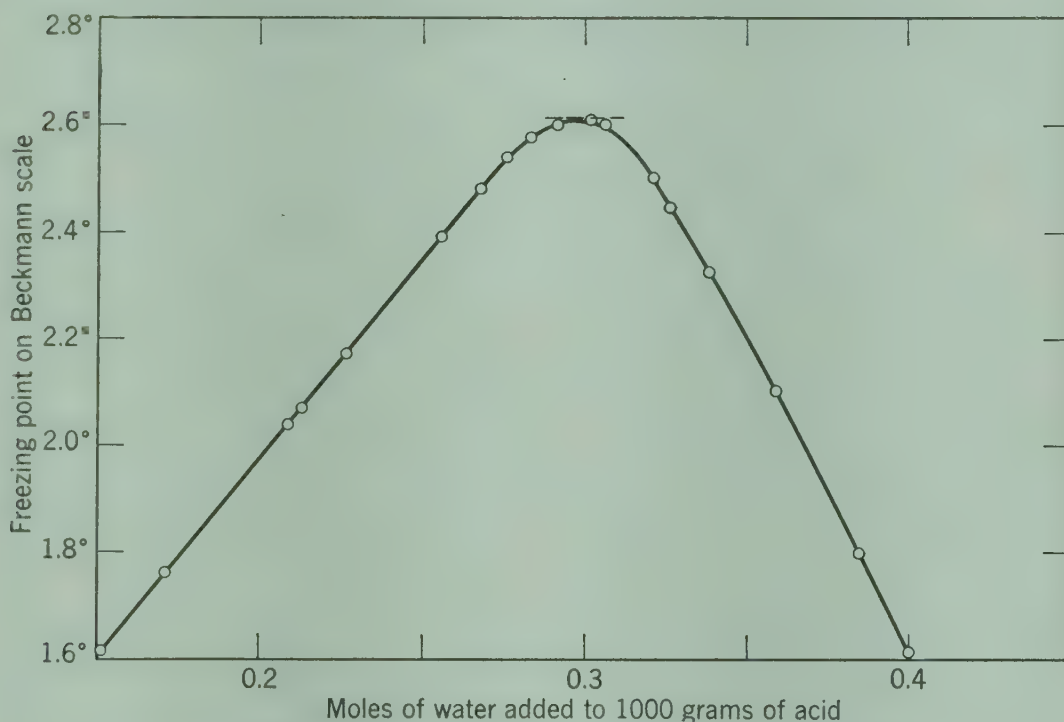
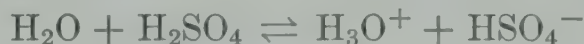


FIGURE 21. Effect of water on the freezing point of sulfuric acid.

The clue to the apparent contradictions in the literature came from the determination of the cryoscopic behavior of water in sulfuric acid as obtained from a study of the $\text{SO}_3\text{--H}_2\text{O}$ system. The freezing point data for this system near the composition of pure H_2SO_4 are plotted in Figure 21. Once the maximum freezing point corresponding to pure H_2SO_4 has been reached, the molal freezing point depression brought about by added water, or the slope of the freezing point curve, after a short interval in which it increases with increasing concentration, becomes constant. The slope of the linear portion of the curve (11.85

(1910); *Ber.*, **55**, 953 (1922); **63B**, 1782 (1930). Oddo and Scandola, *Z. physik. Chem.*, **62**, 243 (1908); **66**, 138 (1909); *Gazz. chim. ital.*, **38**, I, 603 (1908); **39**, II, 1, 44 (1909); **40**, II, 163 (1910). Oddo and Casalino, *Gazz. chim. ital.*, **47**, II, 200, 232 (1917); **48**, I, 17 (1918). Bergius, *Z. physik. Chem.*, **72**, 338 (1910). Poma, *J. chim. phys.*, **10**, 177 (1912). Kendall, Adler, and Davidson, *J. Am. Chem. Soc.*, **43**, 1846 (1921).

degrees per mole) is very nearly that to be expected from a strong binary electrolyte. (The generally accepted value for the molal freezing point of sulfuric acid, as calculated from the heat of fusion, is 6.154 degrees per mole.) The initial curvature at low concentrations of water is attributed to the large self-ionization of the solvent, which gives as one of its products an ion (HSO_4^-) identical with one of those produced by reaction of water:



The self-ionization of sulfuric acid is, according to Hammett and Deyrup, correctly represented by the following equilibria:



The bisulfate ion resulting from the addition of water represses the solvent dissociation; therefore, the increase in solute concentration is less by an amount equal to the number of moles per liter of products disappearing by repression. When repression of solvent dissociation is essentially complete, the linear portion of the freezing point curve is attained. Once this has occurred, further depression of the freezing point will be proportional to the total number of moles produced by the dissociation of the solute.

The contradictory character of many of the earlier data on the cryoscopic and conductivity behavior of solutes, particularly in dilute solution, in sulfuric acid would appear to be attributable, in large part, to neglect in taking into account the high degree of self-dissociation of the solvent. The more recent cryoscopic measurements have therefore been made, using sulfuric acid solutions which contained sufficient water to repress completely the self-ionization of the solvent. The resulting data have thus become consistent and meaningful.

For example, Hammett and Deyrup (11) reexamined the cryoscopic behavior of sodium, potassium, and barium acid sulfates in sulfuric acid and showed that these substances are apparently completely dissociated in this medium. The values obtained for the mole numbers (that is, the van't Hoff factors) for these solutes remain constant even at moderately large ionic strengths. The effect of water on the solubility of barium sulfate in sulfuric acid confirms the picture of sulfuric acid as a solvent in which ions act as nearly ideal solutes. The decrease in solubility of barium sulfate in sulfuric acid in the presence of water is attributed to a common ion effect which arises from the

fact that both solutes are bases in the sulfuric acid system and that both give rise to the characteristic basic ion (HSO_4^-) of the system. On the assumption that barium sulfate is converted to the acid sulfate, the solubility product principle can be applied to an initial electrolyte (BaSO_4) solubility of 0.8 molal and over a range of concentrations of added electrolyte (H_2O) from 0 to nearly 3 molal.

Although early studies on the conductivities of inorganic and organic electrolytes in absolute sulfuric acid had given discordant results, it was apparent that such solutions are excellent conductors and that their equivalent conductances are virtually independent of dilution (8, 12). On the basis of observations on the conductivities of neutral sulfates in absolute sulfuric acid, Kendall, Adler, and Davidson (13) suggested that the contradictions in data reported in the literature are attributable chiefly to the solvent correction which varies from 80 to 90% of the total conductivity. The cryoscopic data obtained by Hammett and Deyrup (11) are in complete harmony with this suggestion.

Little is known concerning the nature of migration phenomena in absolute sulfuric acid. Hantzsch (14) has stated that no ion migration can be demonstrated in this medium. However, the careful work of Hammett and Lowenheim (15) on the determination of the transference number of barium ion in a sulfuric acid solution of the acid sulfate refutes the report of Hantzsch.

Using the Hittorf method of measuring transference numbers and trichloroacetic acid (a non-electrolyte in absolute sulfuric acid) as a reference solute, Hammett and Lowenheim showed that barium ion migrates toward the cathode. However, the extraordinarily low value of approximately 0.007 was obtained for the transference number of this ion. It is impossible to account for the low transference number of the barium ion by postulating that part of the barium is present in solution as an anionic complex. Cryoscopic evidence (11) gives a mole number value of three for barium acid sulfate in sulfuric acid, whereas the existence of part of the barium in the form of an anionic complex would lead to a maximum mole number of one.

The fact that all the bisulfates which have been studied in sulfuric acid possess almost identical conductivities also argues against the existence of an anionic complex. The low value obtained for the transference number of barium ion would appear to explain the identical conductivities of the bisulfates; it is obvious that even large variations in cation mobility will give only small changes in total conductivity when the cation carries less than 1% of the current.

Nor can the small transference of the barium ion be attributed to high mobility of the bisulfate ion in absolute sulfuric acid. In view of the high viscosity of the medium, the magnitude of the changes in concentration of solute in the cathode compartment argues effectively against this possibility.

Hammett and Lowenheim conclude that 99% of the conductance of a solution of the bisulfate ion in absolute sulfuric acid depends on a process other than one of simple ion migration. They suggest that conduction takes place by means of proton jumps between bisulfate ions and adjacent sulfuric acid molecules. The high viscosity of sulfuric acid submerges almost entirely the competition of simple ion migration.

THE NATURE OF SULFURIC ACID SOLUTIONS OF ORGANIC COMPOUNDS

Practically all organic compounds, with the exception of saturated aliphatic and most aromatic hydrocarbons and their halogen derivatives, are soluble in absolute sulfuric acid. Kendall and Carpenter (16) have investigated the solubility of a wide variety of oxygen-containing compounds by the freezing point method. Aliphatic acids, benzoic acid and its homologs, aldehydes, ketones, anhydrides, and phenols form addition compounds with the solvent. They are considered to be true oxonium salts, and their formation is regarded as a manifestation of the basic character of the oxygen-containing organic compounds in absolute sulfuric acid. Consideration of the solvates formed with organic acids serves to emphasize the latter point. With very weak acids (that is, weak with respect to their behavior in water) solvates of the types $\text{RCOOH} \cdot \text{H}_2\text{SO}_4$ and $2\text{RCOOH} \cdot \text{H}_2\text{SO}_4$ are isolated. An increase in acid strength is accompanied by loss of ability to form such addition compounds; for example, *o*-chloro- and *o*-bromobenzoic, chloroacetic, trichloroacetic, and α -chlorocrotonic acids give no indication of compound formation. The effect of acid strength on solvate formation is brought out in Figure 22.

The pioneer investigations of Hantzsch (8, 17, 18, 19) and the later studies of Hammett (11, 20, 21) and of Newman (22) and their collaborators on the cryoscopic behavior of organic compounds in sulfuric acid have shed much light on the nature of such solutions. The data accumulated on the behavior of oxygen-containing compounds have been particularly stimulating to the organic chemist. Almost all oxygen-containing organic compounds are basic in sulfuric acid.

being capable of accepting a proton from the solvent to form an oxonium ion as the conjugate acid and the bisulfate ion:



The oxonium ion may or may not be stable; if it is not stable, it undergoes further reaction with the solvent. On the basis of the mole

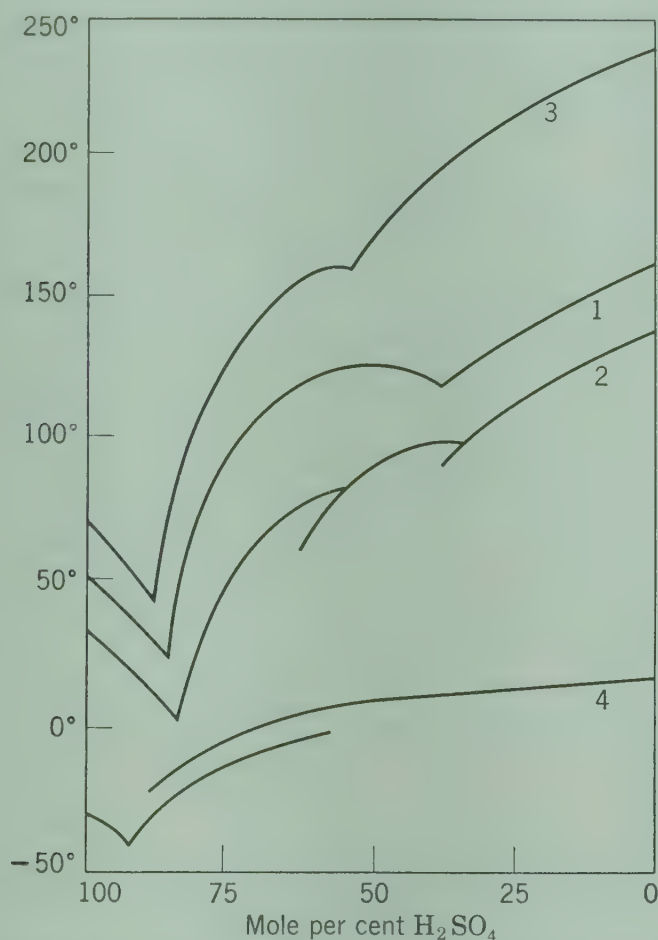


FIGURE 22. Freezing point diagrams for systems: $RCOOH-H_2SO_4$. 1. Benzoic acid. Subtract 40° from temperature scale. 2. *m*-Toluic acid. Subtract 20° from temperature scale. 3. *p*-Toluic acid. Subtract 60° from temperature scale. 4. Trichloroacetic acid. Add 40° to temperature scale.

numbers obtained by cryoscopic measurements, organic substances may be classified according to the types of ionization they exhibit in sulfuric acid.

A few oxygen-containing organic compounds, for example, trichloroacetic acid, *s*-trinitrobenzene, picric acid, and dimethyl sulfate, are unionized in sulfuric acid and give mole numbers of one. Nitrobenzene and dichloroacetic acid give freezing point depressions between one and two times that of a non-electrolyte and would thus appear to be incompletely ionized, whereas monochloroacetic acid gives a mole

number of two. The behavior of the chloroacetic acids is that which would be predicted, since increased substitution by chlorine would be expected to decrease the tendency for the acid to accept a proton from sulfuric acid.

Ethers and most carbonyl compounds undergo "normal" ionization (22) in sulfuric acid, that is, they behave as simple monoacid bases, giving mole numbers of two:

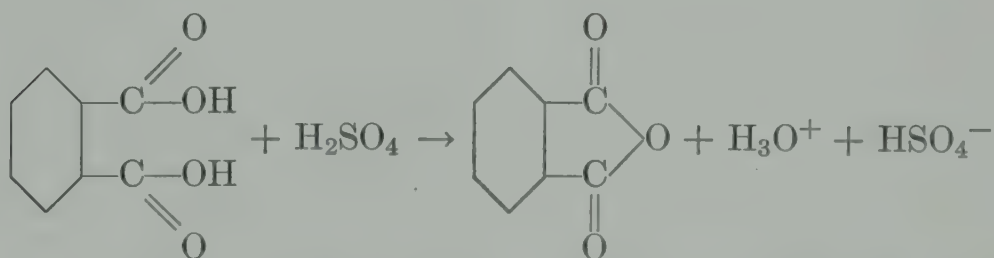


The original solute may be recovered from such solutions by dilution with water.

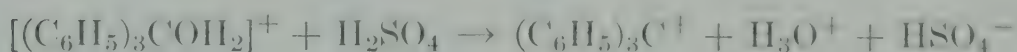
Primary aliphatic alcohols give mole numbers of three, being converted to alkyl sulfuric acids according to the following equation:



Maleic, succinic, and phthalic acids also give freezing point depressions three times that of a non-electrolyte, probably because of anhydride formation.

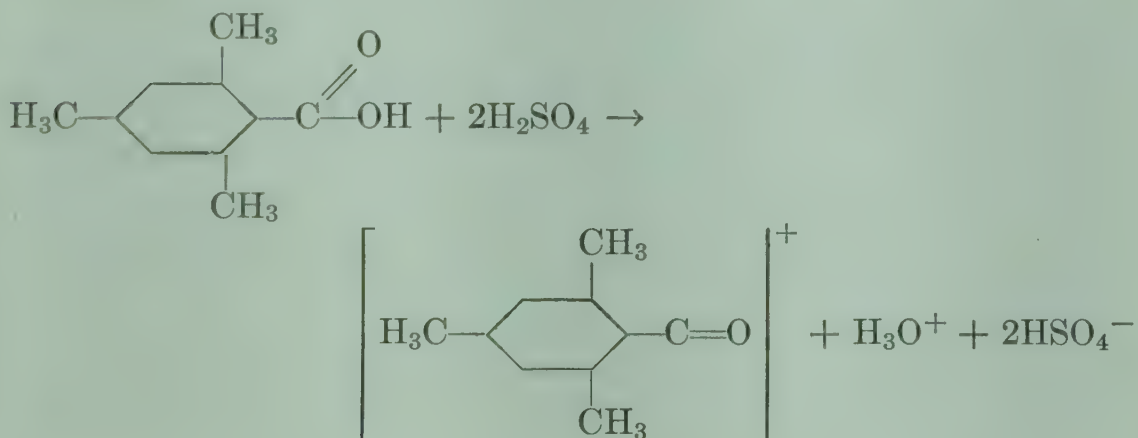


In addition to the types described above, there are many examples of complex ionization (22) in sulfuric acid. In such instances the oxonium ion first formed reacts further with the solvent to form a carbonium ion, and thus mole numbers greater than three are obtained. For example, triphenylmethyl carbinol dissolves in sulfuric acid to give an intensely yellow solution with a molal freezing point depression four times that produced by a non-electrolyte. The following sequence of reactions is believed to be responsible for such a high mole number:

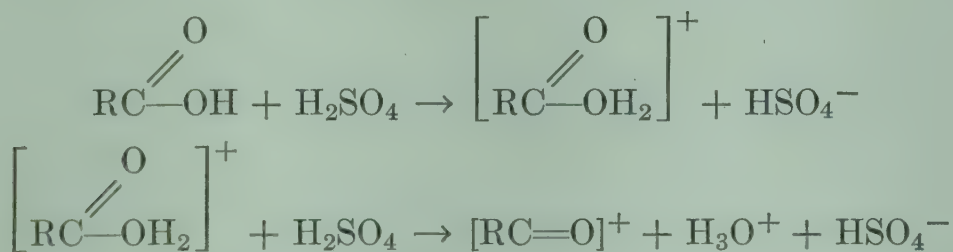


Ionization and Organic Reactions in Sulfuric Acid. The observations of Treffers and Hammett (20) on the complex ionization of

2,4,6-trimethylbenzoic acid and other diortho-substituted benzoic acids have been a considerable stimulus in connection with organic problems of reaction kinetics and mechanism. The acid is found to give a mole number of four in sulfuric acid, presumably as a result of the following reaction:



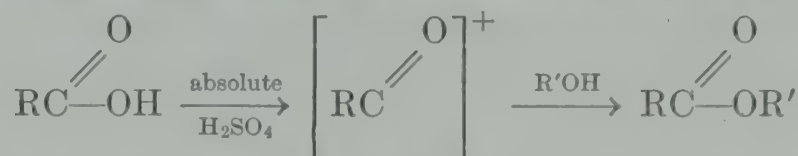
This interpretation is supported by the fact that the methyl ester of the acid, which is a classic example of a sterically hindered ester, is completely hydrolyzed when the absolute sulfuric acid solution is poured into water. Mole numbers for 2,6-dimethylbenzoic and 3,5-dibromo-2,4,6-trimethylbenzoic acids vary between two and four in sulfuric acid, indicating that in these instances the reaction giving the carbonium ion of the acyl type is incomplete and that this reaction occurs in two non-overlapping steps.



Treffers and Hammett showed that acyl ion formation is favored by substitution of ring hydrogen by the methyl group, an electron-releasing group, and is hindered by substitution of electron-attracting groups such as the bromo and nitro groups. They point out that the process of acyl ion formation does not appear to be related to the kinetic steric hindrance which diortho-substituted compounds generally exhibit.

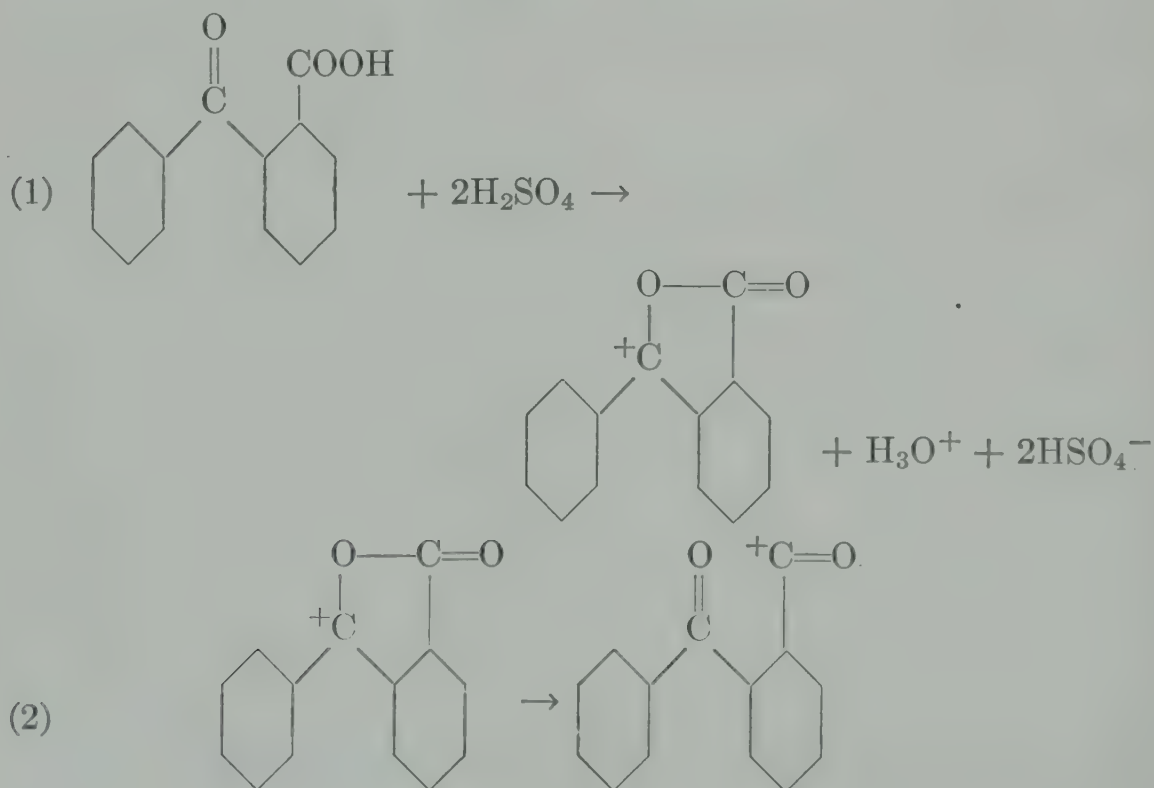
Newman (23) used these observations to devise an extremely rapid method for esterifying certain sterically hindered acids which are

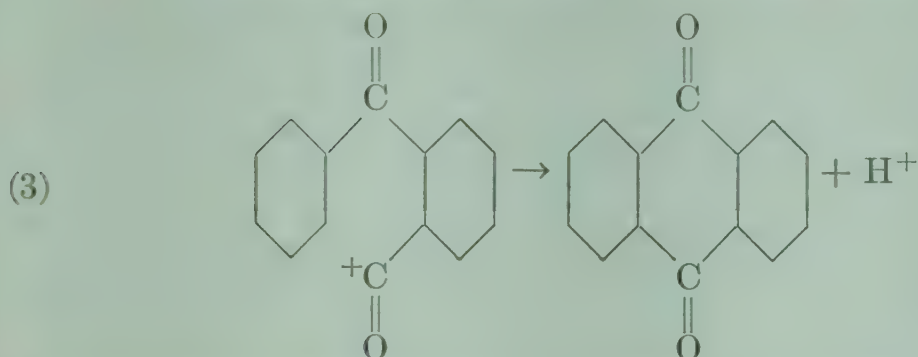
capable of yielding a positive acyl ion in absolute sulfuric acid. The sequence of reactions involved in the esterification is shown below:



Methyl, ethyl, and isopropyl 2,4,6-trimethylbenzoates and methyl 2,4,6-triisopropylbenzoate were prepared in high yields in this manner. Although in principle this procedure is not limited with respect to the alcohol used, Newman was unable to prepare an ester from *tert*-butyl alcohol. The esters prepared as described above could be reconverted to the parent acids in over 90% yield by dissolving them in absolute sulfuric acid and pouring the resulting solution into water. Not all the sterically hindered acids studied could be converted to esters by the procedure outlined; for example, no ester could be obtained from 2,4,6-tribromobenzoic acid. This is not surprising in view of the unfavorable effect of the bromo groups on acyl ion formation.

It was further demonstrated that the unhindered *o*-benzoylbenzoic acid is largely esterified when a solution of this compound in sulfuric acid is poured into methanol. The fact that the pseudo ester is first formed offers, according to Newman (24), a mechanism for the formation of anthraquinone when *o*-benzoylbenzoic acid is dissolved in absolute sulfuric acid and the resulting solution heated. The proposed mechanism is outlined in the equations shown below:





Additional evidence in support of equation 1 of the series shown above is offered by the fact that *o*-benzoylbenzoic acid gives a mole number of four in sulfuric acid.

The formation of a carbonium ion has also been the basis for a postulated mechanism for the Schmidt reactions of acids and of certain esters with hydrazoic acid in sulfuric acid as solvent (25).

The importance of electronic effects on acyl ion formation has been further emphasized by the results of an investigation by Kuhn and Corwin (26) on the cryoscopic and hydrolytic behavior of esters of the

type $\text{RC} \begin{smallmatrix} \text{O} \\ \parallel \end{smallmatrix} \text{OR}'$. A variety of esters, none of which had substituents ortho to the active carbonyl group, was studied. Many of the esters appear to undergo a type of complex ionization differing from that described by Treffers and Hammett and Newman in that acyl ion formation does not appear to be complete as evidenced by the somewhat smaller mole numbers obtained and by the fact that the sulfuric acid

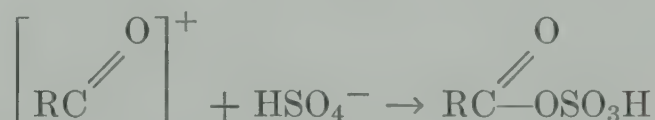
TABLE 59

THE CRYOSCOPIC BEHAVIOR OF SOME ESTERS IN SULFURIC ACID

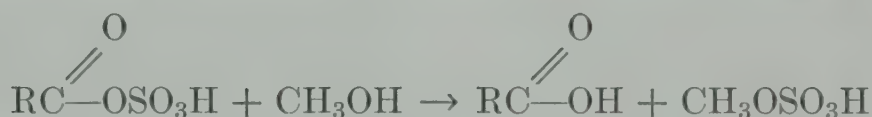
<i>Ester</i>	<i>Mole Number</i> (<i>Approximate</i>)
Ethyl benzoate	2
Chloroethyl benzoate	2.2
Trichloroethyl benzoate	2.8
Cellosolve benzoate	4.3
Cellosolve 3,4-dichlorobenzoate	2.2
Ethyl anisate	3
Chloroethyl anisate	4.4
Ethyl acetate	1.9
Chloroethyl acetate	3
Trichloroethyl acetate	3.5
Chloroethyl chloroacetate	1.8
Cellosolve acetate	5.3
Cellosolve chloroacetate	2.1

solutions always give the free acid when they are poured into alcohol. The mode of ionization (as denoted by mole number) is greatly influenced by the electronic character of both the R and R' groups. Electron-attracting groups in the alcohol part of the ester and electron-repelling groups in the acid portion facilitate acyl ion formation, whereas electron-attracting groups in the acid portion inhibit such reaction. Electronic effects on acyl ion formation are brought out by the data of Table 59.

The fact that certain of the esters yield the free acid rather than the expected methyl ester when poured into cold methanol is explained by the assumption that the intermediate acyl ion is unstable and reacts with a bisulfate ion to give an acyl sulfate:



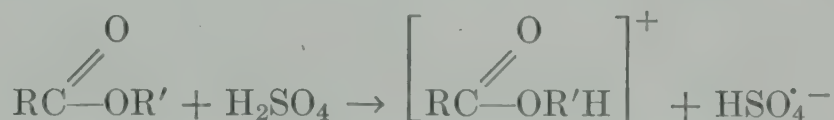
The acyl sulfate then reacts with methanol in the following manner:



Plausibility is lent to the above interpretation by the observation that benzoyl and acetyl sulfates react with alcohols, with the formation of the free acids.

In addition to the effects of the electronic character of R and R'

groups in $\text{RC} \begin{array}{c} \text{O} \\ // \\ \end{array} \text{OR}'$, the basicity of the ester itself is of importance in acyl ion formation. The ester may be so weak a base that the first step

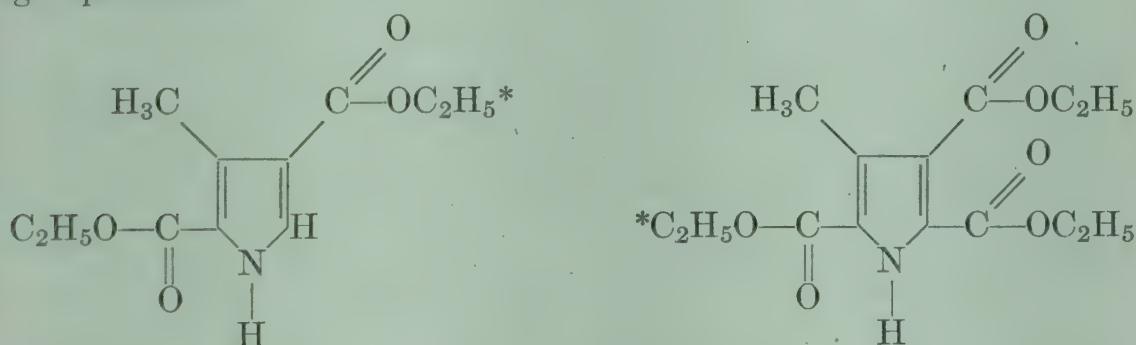


in the sequence of reactions involving acyl ion formation cannot take place. The freezing point data (Table 59) demonstrate that such a situation prevails in cellosolve chloroacetate and cellosolve 3,4-dichlorobenzoate. The mole number value for each of these substances is approximately two, a fact which indicates that the chlorine atoms in the acid portion of the ester and the oxonium ion in the cellosolve portion weaken the basicity to an extent preventing the primary step of proton transfer to the carbonyl group.

Fischer and Walach (27) have shown that the hydrolysis of a sulfuric acid solution of Knorr's pyrrole (2,4-dimethyl-3,5-dicarbethoxy-

pyrrole) which has been kept at 35°C. results in the selective conversion of the β -carbethoxy to a carboxyl group. An investigation of this reaction by Corwin and Straughn (28) indicates that this selective hydrolysis may be attributed to conversion of the pyrrol carboxylic ester to an acyl ion in sulfuric acid. The ester gives a mole number of three and one-half in sulfuric acid, as determined by freezing point depression measurements, indicating incomplete acyl ion formation. Moreover, when the β -acid formed upon hydrolysis is dissolved in absolute sulfuric acid and poured into methanol, about one-third of the product recovered is ester.

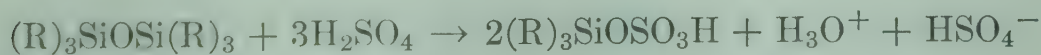
The behavior of other pyrrol carboxylic esters shows that in this series, just as in the benzene series, steric crowding of the ester group concerned and the presence of electron-repelling groups on the ring favor acyl ion formation. The inherent electron-donating power of the nitrogen in the pyrrole ring is itself an important factor in promoting acyl ion formation. Two pyrrol esters which were found to yield acyl ions in sulfuric acid had only one group adjacent to the reactive ester group. These are shown below with the active ester groups starred.



Newman, Craig, and Garrett (29) have studied the cyroscopic behavior of several organo-silicon compounds in sulfuric acid. Triethylsilanol approximates the behavior of primary alcohols in this solvent, giving a mole number of three:

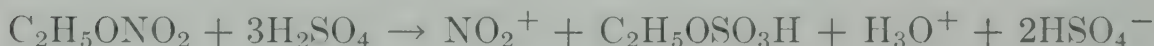


Hexamethyldisiloxane, hexaethyldisiloxane, and triethylethoxysilicon yield mole numbers of approximately four, probably in accordance with the following reactions:



Treatment with water of the sulfuric acid solutions of the various organo-silicon compounds mentioned above yields the disiloxanes. Reaction of the acid solutions with ammonium chloride results in the precipitation of the trialkylsilicon chlorides in excellent yields, presumably as a result of interaction of the halide ion with the trialkyl-silicon acid sulfate which is common to all the solutions.

Absolute nitric acid and ethyl nitrate undergo complex ionization in sulfuric acid, giving mole numbers of four (17) and five (30), respectively. Since such solutions are exceedingly powerful nitrating agents for aromatic compounds, attention has been directed toward the nature of their complex ionization with the hope of elucidating the mechanism of the nitration reaction. The following reactions have been postulated for the ionization of nitric acid and ethyl nitrate in solvent sulfuric acid:



Considerable evidence, in addition to the mole number values cited above, is available to support the validity of the proposed complex ionization reactions. This evidence (30, 31) is summarized below.

1. Ethyl nitrate is obtained when a solution of nitric acid in absolute sulfuric acid is poured into cold ethanol; nitric acid is recovered when a solution of the ester in sulfuric acid is poured into water at 0°C.

2. The ultraviolet absorption frequencies characteristic of the nitrate ion and nitric acid are absent or very much diminished in solutions of absolute nitric acid in sulfuric acid. The spectrum of ethyl nitrate in sulfuric acid is almost identical with that of nitric acid in the same solvent; the spectrum of the former substance in sulfuric acid is different from that of its solution in an inert solvent such as chloroform.

3. The partial pressure of nitric acid dissolved in 98% sulfuric acid is negligible.

4. Solutions of nitric acid in absolute sulfuric acid have a high electrical conductivity. Upon electrolysis of such solutions nitric acid migrates toward the cathode.

5. A Raman shift, $\Delta\nu = 1400 \text{ cm}^{-1}$, can be detected in absolute nitric acid; this shift is stronger in nitric-sulfuric acid mixtures. The intensity of this shift increases with the sulfuric acid content of the mixture. The frequency observed cannot be attributed to the nitric acid molecule, the nitrate ion, or to nitrogen pentoxide.

6. The ionization pictured for nitric acid and for ethyl nitrate helps to give a quantitative interpretation of the kinetics of nitration of aromatic nitro compounds (31, 32). The NO_2^+ ion is considered to be the active nitrating agent.

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HYDROGEN FLUORIDE

Despite the difficulties and hazards involved in the handling of anhydrous hydrogen fluoride, there is no other inorganic non-aqueous solvent which has been studied so intensively within recent years. As a result, hydrogen fluoride is now a solvent of considerable importance for a variety of organic reactions. Up to the present, however, its usefulness as a medium for inorganic reactions has been considerably limited in scope.

Hydrogen fluoride has been known for many years, having been prepared first by Margraff (1) in 1768 and definitely characterized by Scheele (2) in 1771. The anhydrous material was first obtained by Frémy (3) by the thermal decomposition of pure, dry potassium hydrogen fluoride. This method still serves as the laboratory process for the preparation of the very pure material and has been the subject of considerable study (4, 5, 6, 7). In the most generally used procedure devised by Simons (4, 7), fused potassium hydrogen fluoride is first electrolyzed in a copper, nickel, or Monel metal vessel to eliminate the last traces of water. The anhydrous potassium hydrogen fluoride is then heated to 500° to 600°C. to yield a rapid stream of pure hydrogen fluoride.

The industrial preparation of hydrogen fluoride involves reaction between high-quality fluorspar and concentrated sulfuric acid at elevated temperatures (300° to 800°C.), followed by condensation of the gaseous products formed (8, 9). Fluosulfonic acid, phosphoric acid, or acid sulfates may be used in place of sulfuric acid. The hydrogen fluoride is stored in all-steel tanks. Commercial hydrogen fluoride contains as impurities less than 0.5% water, less than 0.1% silicon tetrafluoride, and a small amount of sulfur dioxide. Water may be removed by treatment with either fluorine or thionyl chloride, the latter being effective by virtue of the following reactions:



If desired, sulfur dioxide may be removed by fractionation. This, however, is seldom done since sulfur dioxide does not interfere with most of the reactions for which hydrogen fluoride is used as a solvent.

Although anhydrous hydrogen fluoride is an extremely hazardous chemical, techniques and precautions for its manipulation have been so well developed that it is now used in large-scale industrial processes (10, 11). The use of rubber gloves is a necessity for handling hydrogen fluoride, since accidental spillage and contact of the acid with the skin lead to a penetrating necrosis which is accompanied by great pain. First-aid treatment for such burns consists of washing the area affected with a calcium hydroxide suspension, and following that with application of a glycerol-magnesium oxide paste or a magnesium stearate ointment. For very severe burns, a subcutaneous injection of calcium gluconate-lactobionate should be made as soon as possible. This treatment neutralizes the acid and causes the precipitation of fluoride ion. Hydrogen fluoride gas irritates the mucous membranes; extended exposure to it causes mild burns on the sensitive areas of the skin. It is necessary, therefore, that all manipulations be carried out within an efficient hood and that the worker be protected by an effective mask.

Hydrogen fluoride readily attacks siliceous substances; therefore, the use of such materials as silicon, cast irons, stoneware, and glass as containers must be avoided. However, quartz has been used for reactions in which the time of contact is short; hydrogen fluoride dissolves quartz to the extent of about 1% in 4 hours. Stainless steel and copper vessels are suitable for handling the anhydrous acid up to temperatures of 200°C. Wrought Monel metal is probably the most widely used metallic material for fabrication of containers in which reactions with hydrogen fluoride are to be carried out. This material is resistant to attack by the acid over a wide temperature range. For exact laboratory work, such as conductance and solubility measurements, only platinum and platinum-gold alloy containers have proved suitable (10, 11).

The great dehydrating power of liquid hydrogen fluoride makes most organic substances unsuitable as materials of construction for its storage. However, Teflon, a tetrafluoroethylene polymer (12), and Kel-F, a trifluoroethylene polymer (13), are resistant to attack by hydrogen fluoride.

Liquid hydrogen fluoride resembles water and hydrogen cyanide to a much greater extent than it does the other hydrogen halides. Its physical properties are distinctly abnormal when the general trends observed for the other hydrogen halides are considered. These anomal-

The dissolution of salts, other than fluorides, is accompanied by extensive, and frequently visible, solvolysis. The chlorides, bromides, and iodides of the alkali metals dissolve with the liberation of the respective hydrogen halides, which are relatively insoluble in liquid hydrogen fluoride. Potassium cyanide dissolves with the evolution of

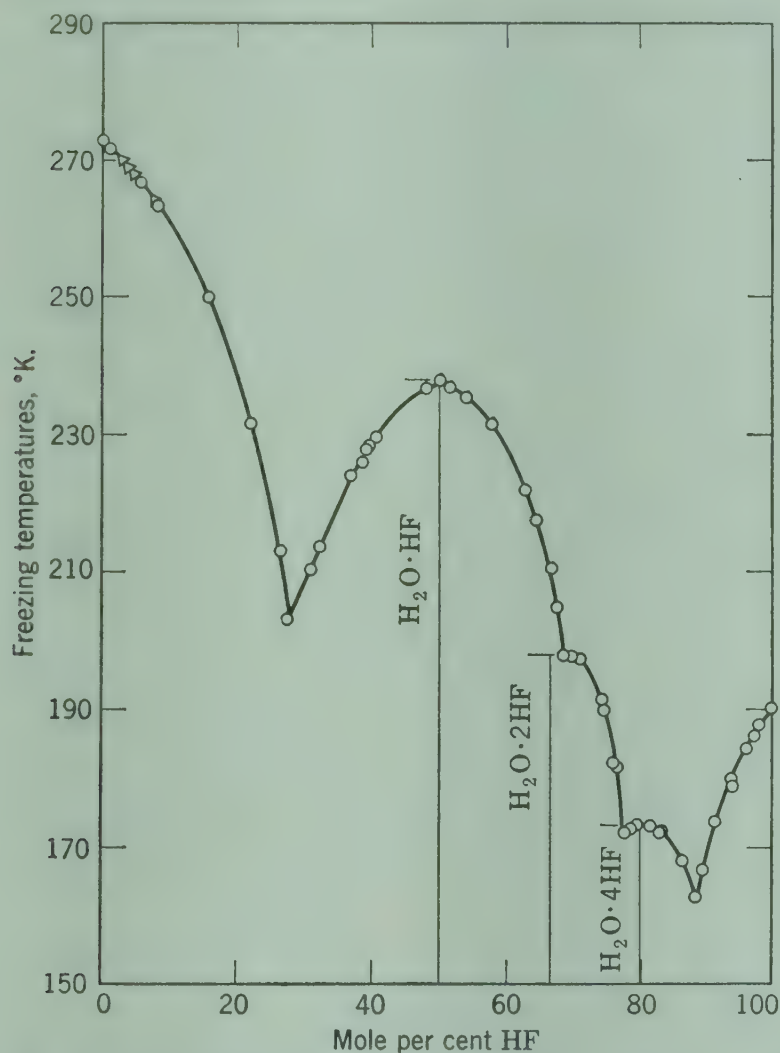


FIGURE 23. Freezing points of aqueous solutions of hydrogen fluoride.

hydrogen cyanide, a substance which on the basis of its similarity to hydrogen fluoride in boiling point and dielectric constant would be expected to be extremely soluble. Many oxides and hydroxides react with liquid hydrogen fluoride. The carbonates of calcium, zinc, and lead yield carbon dioxide on contact with hydrogen fluoride. The qualitative solubilities of a large number of inorganic compounds in liquid hydrogen fluoride are summarized in Table 61. Quantitative data are given wherever they are available. Where visible reaction occurs, the reaction products which have been identified are shown in parentheses.

TABLE 61
THE SOLUBILITY OF INORGANIC COMPOUNDS IN LIQUID HYDROGEN FLUORIDE

Very Soluble	Slightly Soluble	Not Appreciably Soluble	Soluble with Reaction	React to Give Insoluble Product	Insoluble and Unreactive
H_2O NH_4F LiF (2.6 g./100 cc. of solution at $18^\circ\text{C}.$) KF (38 g./100 cc. of solution at $0^\circ\text{C}.$) RbF CsF TlF AgF (33 g./100 cc. of solution at $-15^\circ\text{C}.$) KClO_4 (9.6 g./100 g. of solution) $\text{Hg}(\text{CN})_2$ (no evolution of HCN) KNO_3 NaNO_3 AgNO_3 K_2SO_4 Na_2SO_4 $\text{NaC}_2\text{H}_3\text{O}_2$ $\text{KC}_2\text{H}_3\text{O}_2$ $(\text{NH}_4)_2\text{S}_2\text{O}_8$ $\text{K}_2\text{S}_2\text{O}_8$	MgF_2 CaF_2 SrF_2 BaF_2 CaSO_4 H_2S CO CO_2	AlF_3 ZnF_2 FeF_3 PbF_2 CuF_2 HgF_2 HCl HBr HI SiF_4 $\text{Cu}(\text{NO}_3)_2$ $\text{Bi}(\text{NO}_3)_3$ $\text{Pb}(\text{NO}_3)_2$ $\text{Co}(\text{NO}_3)_2$ ZnSO_4 CdSO_4 CuSO_4 Ag_2SO_4	Alkali and alkaline earth metal halides dissolve with the evolution of hydrogen halides $\text{KCN}(\text{HCN})$ $\text{NaN}_3(\text{HN}_3)$ $\text{K}_2\text{SiF}_6(\text{SiF}_4)$ $\text{KClO}_3(\text{ClO}_2)$ Ag_2O $\text{K}_2\text{Cr}_2\text{O}_7(\text{CrO}_2\text{F}_2)$ KMnO_4 (oxyfluoride containing heptapositive manganese)	$\text{AlCl}_3(\text{HCl})$ $\text{FeCl}_2(\text{HCl})$ $\text{MnCl}_2(\text{HCl})$ $\text{CeCl}_3(\text{HCl})$ MgO CaO BaO BaO_2 CuO	Hydrogen halides ZnCl_2 SnCl_2 NiCl_2 CdCl_2 CuCl CuCl_2 HgI_2 HgCl_2 AgCl AgBr AgI HgO PbO_2 MnO_2 SnO_2 Cr_2O_3 WO_3 Mn_2O_3

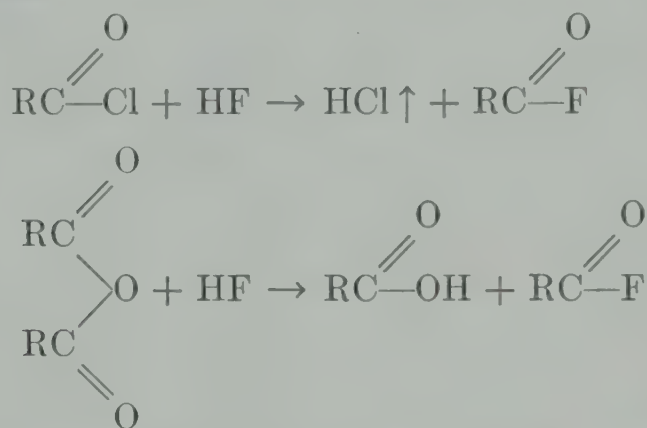
SOLUBILITY OF ORGANIC COMPOUNDS (22, 29). The solvent power of liquid hydrogen fluoride for organic compounds is unusually great. Characteristically, organic substances are either very soluble or practically insoluble in this solvent. Here, as with the alkali metal fluorides, high solubility appears to parallel compound formation with the solvent. Saturated hydrocarbons, their halogenated (other than fluoro) derivatives, and thiophenols are insoluble, whereas unsubstituted aromatics are usually only slightly soluble. In general, the solubility of substituted aromatic hydrocarbons is dependent on the nature of the substituent. Aromatic as well as aliphatic compounds are with few exceptions (for example, diphenyl derivatives) soluble if they possess substituents containing nitrogen, sulfur, or oxygen atoms, or the olefinic grouping, all of which are capable of acting as donor groups for onium compound formation with hydrogen fluoride.* The presence of electron-withdrawing groups, such as the halogen or nitro groups on an aromatic nucleus generally has a marked depressing effect on solubility. Thus, whereas phenols are soluble, mononitrophenols possess only limited solubility, and trinitrophenol is insoluble. Bromobenzoic acid is insoluble, but the unsubstituted acid is extremely soluble. It should be noted, however, that although the solubility of benzene is quite limited, that of nitrobenzene is high. In this case the nitro substituent appears to be capable of acting as a donor group.

The solubility of such aromatic hydrocarbons as benzene, toluene, anthracene, *o*- and *m*-xylene, and tetralin is considerably increased by the addition of mercury(II) cyanide or azide, silver(I) fluoride or azide, or thallium(I) fluoride (29). Except for thallium(I) fluoride the normal solubility of the hydrocarbons is increased by an additional four moles for each formula weight of salt added. To account

*It has been proposed that hydrogen fluoride be used as a selective solvent for removal of sulfur compounds from petroleum stocks. It is interesting in this respect that the degree of extraction of individual sulfur compounds shows an orderly progression with changes in the type of sulfur linkage, in molecular weight, or in configuration of substituent groups. Increased solubility is obtained in going from mercaptans to disulfides to thioethers; decrease in extent of extraction is observed with increasing molecular weight of a given type of sulfur compound. Transition from primary to tertiary alkyl substituents results in increased extraction, whereas introduction of the phenyl group results in a marked lowering of solvent action. It is apparent that these observations may readily be interpreted in terms of increasing solubility with increasing basic character of the sulfur compound. The solubility of slightly soluble phenyl sulfide is markedly increased by the addition of boron trifluoride, a substance which behaves as an acid (see section on reactions involving acid-base relationships) in liquid hydrogen fluoride. [Lien, McCauley, and Evering, *Ind. Eng. Chem.*, **41**, 2698 (1949).]

for this phenomenon, the formation of complexes of the composition $(M\text{Ar}_4)\text{X}$ has been postulated. Such complex compounds could not be isolated, however; evaporation of the hydrocarbon solutions resulted in the recovery of unchanged metal salt.

Acid halides and anhydrides undergo complete solvolysis when they are dissolved in liquid hydrogen fluoride. The acid fluoride is formed in these instances.



THE NATURE OF HYDROGEN FLUORIDE SOLUTIONS (22, 24, 29, 30, 31). Solubility, boiling point, and particularly conductivity investigations

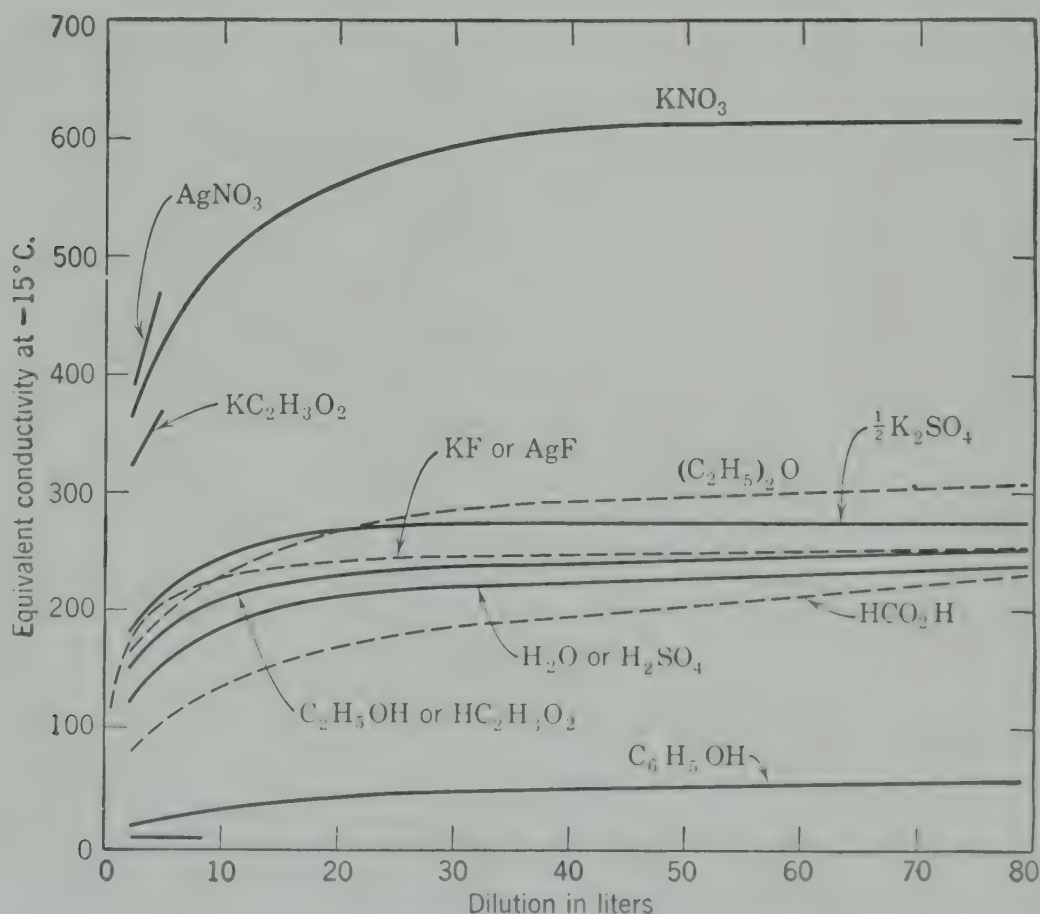
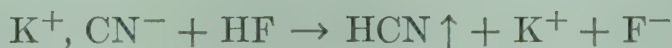


FIGURE 24. Conductivities in liquid anhydrous hydrogen fluoride.

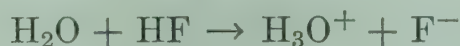
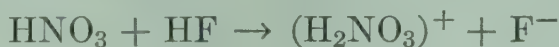
indicate that dissolution of inorganic and organic compounds in liquid hydrogen fluoride is generally accompanied by reaction between dissolved substance and solvent. The graphic summary in Figure 24 of the conductivity data of Fredenhagen and Cadenbach (22, 30, 31) reveals that the following types of behavior are possible when a substance is dissolved in liquid hydrogen fluoride.

1. Normal dissociation into ions may take place. This is the behavior exhibited by the simple fluorides. These substances appear to be completely dissociated in the more dilute solutions. Solution of these substances is undoubtedly accompanied by solvation of the fluoride ion with the formation of HF_2^- and other more complex anions.

2. The solution process may involve a solvolytic reaction of the type

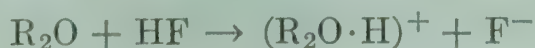
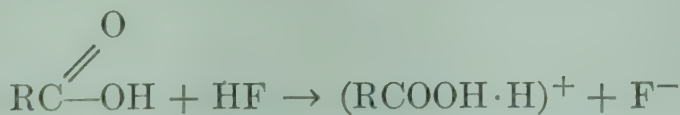


The initial solvolytic process may be followed by a secondary reaction involving the solvent. This type of behavior accounts for the high conductivity values of such salts as nitrates, acetates, and sulfates.



The secondary reactions involving proton transfer from solvent to one of the products of solvolysis are manifestations of the highly acid nature of hydrogen fluoride.

3. The process of solution may involve the addition of hydrogen fluoride to the solute, followed by the dissociation of the solvate into a complex cation and the fluoride ion. Water and most organic compounds (acids, alcohols, ethers, etc.) containing groups which are potentially donors of electron pairs appear to dissolve in this manner.



4. The solute may dissolve to give a non-conducting or poorly conducting solution. This type of behavior is limited to organic substances which are, by virtue of their structures, only weakly basic, that is, they are poor proton acceptors, in liquid hydrogen fluoride. For example, phenol and trichloroacetic acid are readily soluble in hydrogen fluoride, both forming solutions which are extremely poor conductors. Acid fluorides are also very soluble, but their solutions are non-conducting.

A few additional remarks concerning the nature of solutions of hydroxy compounds in liquid hydrogen fluoride are pertinent at this point. An alternative possibility (to that shown above) to account for the fact that monohydroxy aliphatic alcohols act as binary electrolytes in hydrogen fluoride would be that they react with the solvent to form a fluoride and water. This alternative does not appear to be reasonable since it has been demonstrated (29) that the reverse reaction actually takes place in liquid hydrogen fluoride. Concepts regarding ionization of polyhydroxy compounds, both of the aliphatic and aromatic types, are not simple. The nature of the ionization reaction appears to be dependent on both the number and the arrangement of the hydroxyl groups (29, 31). Moreover, the matter is considerably complicated by the possibility of molecular rearrangement of the solute (31).

INORGANIC REACTIONS IN LIQUID HYDROGEN FLUORIDE

METATHETICAL REACTIONS. Because of the extensive solvolysis which ionic salts undergo in liquid hydrogen fluoride, anions other than the fluoride ion can be present only in limited quantity in this medium. Metathetical reactions, therefore, are of minor significance in hydrogen fluoride. However, the fact that some reactions involving metathesis do take place demonstrates that solvolysis is by no means complete.

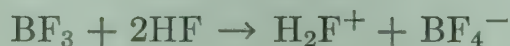
Fredenhagen (24) has shown that the appropriate silver(I) or thallium(I) halide is slowly precipitated when hydrogen chloride, bromide, or iodide gas is passed through a hydrogen fluoride solution containing either silver(I) or thallium(I) ion. A similar precipitation takes place upon mixing cold solutions of a silver(I) salt and freshly prepared alkali metal chloride. If the chloride solution is kept at 10°C. for some time, solvolysis occurs to such an extent that silver(I) chloride can no longer be precipitated. It is possible by precipitation re-

actions to show also the existence in anhydrous hydrofluoric acid of small concentrations of the perchlorate, periodate, and sulfate ions.

REACTIONS INVOLVING ACID-BASE RELATIONSHIPS (32). Anhydrous hydrogen fluoride is a highly acid solvent in which auto-ionization, as shown by the equation given below, occurs to a relatively large extent.



This high acidity limits considerably the number of substances capable of acting as acids in hydrogen fluoride. Indeed, there are no known compounds which can behave as acids in the Brönsted sense. There are, however, a number of derivatives of hydrogen fluoride which exhibit acidic behavior in this medium, in the sense that they can compete successfully with the proton for a share in the electrons of the fluoride ion and thus increase the concentration of fluoronium ion, H_2F^+ , in solution. This reaction is illustrated below with boron trifluoride:



Qualitatively, for fluorides to compete successfully for a share in the electrons of the fluoride ion they must fulfill the following requirements: (a) They must possess a central atom with orbitals available for binding fluoride ions; (b) the valence state of the central atom must be high; and (c) the geometrical factors (for example, the radius ratio of the central atom to fluorine atom) must be such as to permit the central atom to increase its coordination number.

The chemical behavior in anhydrous hydrogen fluoride of a large number of fluorides has been studied by Clifford (32) in an attempt to evaluate their ability to behave as acids. The following experimental criteria were used to determine relative acid strengths.

1. Solubility. Low solubility indicates low affinity for the fluoride ion.

2. Solvent power on various metallic (basic) fluorides. The following metallic fluorides, arranged in order of increasing basicity, were employed: (CoF_3 , MnF_3 , CrF_3), HgF_2 , AgF_2 , CuF_2 , (NiF_2 , CoF_2), CaF_2 , AgF , and NaF .

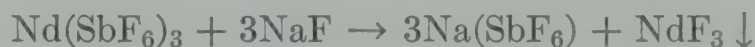
3. Solvent power on various metals. The following metals, arranged in order of increasing electropositivity, were used: Ag, Hg, Cu, Pb, Sn, Nb, Cr, Zn, Mn, Mg, and Ca.

Antimony(V) fluoride was found to be the strongest acid of the various fluorides studied. It dissolves in liquid hydrogen fluoride,

with the evolution of considerable heat. The resulting solution, presumably containing fluoantimonic acid, $\text{H}(\text{SbF}_6)$, is capable of dissolving mixed ignited rare-earth oxides slowly, and simple rare-earth fluorides rapidly. The latter reaction is believed to involve a simple neutralization in accordance with the illustrative equation shown for neodymium fluoride.



The addition of sodium fluoride (a strong base) to the solution results in the precipitation of the rare-earth fluoride.



Fluoantimonic acid dissolves metallic copper, forming a yellow solution presumably containing $\text{Cu}(\text{SbF}_6)_2$. It is the only acid studied which proved to be capable of dissolving the very weak base cobalt(III) fluoride.

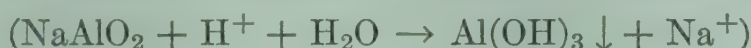
Fluoarsenic acid, $\text{H}(\text{AsF}_6)$, and fluophosphoric acid, $\text{H}(\text{PF}_6)$, were prepared by the fluorination of the corresponding elements in hydrogen fluoride by means of chlorine trifluoride. On the basis of their reactions these acids are weaker than fluoantimonic acid, the acid strength diminishing in the order $\text{H}(\text{SbF}_6) > \text{H}(\text{AsF}_6) > \text{H}(\text{PF}_6)$. A solution of fluoarsenic acid vigorously attacks magnesium, manganese, mercury, and lead, but has no action on copper. It fails to dissolve cobalt(II) or copper(II) fluoride, but produces a white precipitate with silver(I) fluoride. Fluophosphoric acid is unreactive towards metallic calcium, magnesium, and tin, although it dissolves silver with effervescence. It gives no apparent reaction with various mercury, cobalt, and manganese fluorides, but dissolves silver(I) fluoride.

Another acid of considerable strength is fluoboric acid, $\text{H}(\text{BF}_4)$, which is prepared by bubbling boron trifluoride into anhydrous hydrogen fluoride. Magnesium and manganese react vigorously with fluoboric acid; these reactions are immediately quenched by the addition of the strong base, sodium fluoride. Copper(II) and silver(I) fluorides react with solutions of fluoboric acid to give yellow and white precipitates, respectively; sodium and potassium fluorides yield clear solutions.

The acid properties of a variety of other fluorides in anhydrous hydrogen fluoride were also investigated. Solutions of germanium(IV), tin(IV), selenium(IV), tellurium(VI), iodine(V), vanadium(V), niobium(V), molybdenum(VI), and tungsten(VI) fluorides exhibit definite but rather low acidity. Titanium(IV) fluoride is very feebly acidic, whereas silicon(IV) fluoride and chlorine(III)

fluoride possess practically no acidic characteristic in hydrogen fluoride.

It is noteworthy that aluminum and chromium(III) fluorides are amphoteric in anhydrous hydrogen fluoride, thus behaving similarly to their hydroxy analogs in water. Cryolite, $\text{Na}_3(\text{AlF}_6)$, which may be looked upon as a salt formed by the combination of the base, sodium fluoride, with the acid, aluminum fluoride, is quite soluble in anhydrous hydrogen fluoride. However, the addition of the acid, boron trifluoride, to such a solution results in the precipitation of aluminum fluoride:



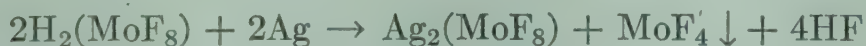
Potassium hexafluorochromate(III), which is also soluble in hydrogen fluoride, undergoes solvolysis, with the precipitation of green chromium(III) fluoride. This precipitate dissolves in an excess of sodium fluoride, with the formation of a green solution:



The addition of boron trifluoride to this solution causes the reprecipitation of the simple fluoride:



During the course of the investigation of the acids of the hydrogen fluoride system, it was noticed that several fluo acids attack silver, mercury, or tin, although these same acids have no effect upon the more electropositive elements, magnesium and calcium. This is explained by the observation that such reaction with the less electropositive metals is unaccompanied by hydrogen evolution and is displayed only by those fluorides capable of undergoing reduction. Probable reactions involving some typical oxidation-reductions are shown below:



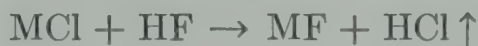
SOLVOLYTIC REACTIONS. The earlier discussion of the solubility of inorganic compounds in liquid hydrogen fluoride emphasized the importance of solvolytic reactions in this medium. This tendency for the solvent to enter into reaction has been utilized for the convenient preparation of several fluo compounds.

Lange and Livingston (33) have described the preparation of anhydrous monofluophosphoric acid, $\text{H}_2\text{PO}_3\text{F}$, in quantitative yield by reaction between anhydrous metaphosphoric acid and liquid hydrogen fluoride. Reaction between 100% orthophosphoric acid and liquid hydrogen fluoride in equimolar ratio results in the establishment of the following equilibria:



Of the orthophosphoric acid 60% is converted to the monofluo acid and only 7% to the difluo acid.

Woyski (34) has devised an effective method for the preparation of sodium, potassium, and ammonium hexafluorophosphates, involving the solvolysis of the metal chlorides and phosphorus(V) chloride and the subsequent combination of the fluorides so formed:



The reactions are carried out in a stainless steel vessel at the temperature of an ice-salt bath and give substantially theoretical yields of the hexafluorophosphates. Woyski (35) has also prepared alkali metal fluosulfonates in good yield by the addition of chlorosulfonic acid to a solution of an alkali metal chloride or fluoride in liquid hydrogen fluoride.

ORGANIC REACTIONS IN LIQUID HYDROGEN FLUORIDE (11) *

Liquid hydrogen fluoride is an important solvent, on both a laboratory and an industrial scale, for a variety of organic reactions. The following factors (8) contribute to its superiority over other reagents which may be used to obtain the same products: (a) the high solvent

* The extensive use of hydrogen fluoride in organic reactions, both as a solvent and as a participant, has been thoroughly and excellently discussed by Wiechert in a chapter in *Newer Methods of Preparative Organic Chemistry*, Interscience Publishers, New York, 1948. For the sake of completeness, however, that portion of the topic which is concerned primarily with the use of hydrogen fluoride as a solvent will be dealt with in a general fashion here. Unless otherwise noted, Wiechert is the source of information concerning this subject.

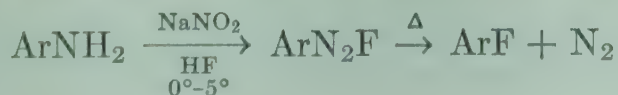
power for many types of organic compounds; (b) high acidity; (c) powerful dehydrating action; (d) inability to dissolve the hydrogen halides; and (e) the great tendency to form molecular complexes. Moreover, its use as a solvent frequently minimizes the extent to which side reactions occur.

In addition to these favorable characteristics, hydrogen fluoride possesses a number of physical properties which make its employment on a commercial scale particularly advantageous (8). The low formula weight gives a more effective chemical per pound than any of the other solvents used for similar organic reactions; this also permits the use of smaller containers and equipment. Hydrogen fluoride may be handled conveniently as a gas or a liquid and may be stored at high concentrations without the development of excessive pressures. Its high fluidity and low surface tension permit the liquid to flow rapidly. Moreover, it may be removed conveniently from the site of reaction by distillation and thus recovered readily.

The following common types of organic reactions have been carried out successfully and conveniently in liquid hydrogen fluoride: fluorinations, diazotizations, nitrations and sulfonations, molecular rearrangements, and oxidations. They are discussed in some detail below.

FLUORINATION REACTIONS. The inertness of hydrogen fluoride towards elementary fluorine makes it an extremely favorable medium in which to perform a variety of fluorination reactions. Fluorinations in this solvent have been effected at temperatures from -70° to $70^{\circ}\text{C}.$, depending upon the nature of the reactants, a pressure high enough to keep the products in the liquid state being maintained. Iodine, antimony, and various heavy metal halides, in proportions of 0.1 to 5%, may be used as catalysts. The absence of moisture is essential since reaction between water and fluorine produces some ozone which may bring about the subsequent oxidation of the organic substances. Among the compounds which have been fluorinated successfully in this manner are aliphatic hydrocarbons and ethers, aromatic hydrocarbons and their halogen, nitro and amino derivatives, carboxylic and sulfonic acids, and pyridine and quinoline.

DIAZOTIZATION REACTIONS. A simple method for obtaining many aromatic fluorides in good yield involves the diazotization in anhydrous hydrogen fluoride of the corresponding amines, and the thermal decomposition of the solutions of the diazonium fluorides so formed:



A large excess of hydrogen fluoride is required since two moles of water are formed for each mole of amine diazotized. An extensive study (36) of this method has shown that for certain amines yields are obtained which are as good or better than those achieved for the same compounds by the familiar Schiemann reaction, in which the diazonium fluoborates are isolated and then decomposed thermally. It is of interest that *o*-fluorobenzoic acid and *m*-fluorophenol may be prepared directly from the corresponding amines, in contrast to the results obtained from the Schiemann reaction. However, satisfactory results cannot be obtained with many ortho-substituted amines, presumably because the diazotized solutions cannot be heated sufficiently high under reflux to cause decomposition of the diazonium fluorides.

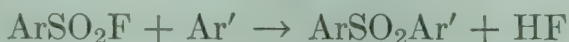
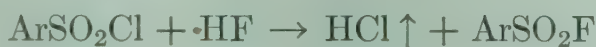
NITRATION AND SULFONATION REACTIONS. Liquid hydrogen fluoride has proved to be a highly suitable medium for effecting the nitration and sulfonation of aromatic compounds. The mono-nitration of benzene in over 80% yield has been accomplished by means of a solution of 100% nitric acid in liquid hydrogen fluoride at 0°C.; no dinitrobenzene is formed. The reaction, however, is a difficult one to carry out since absolute nitric acid reacts violently with hydrogen fluoride. The nitration may be performed more readily by means of solutions of potassium nitrate in hydrogen fluoride. Because of extensive solvolysis, potassium nitrate, when dissolved in hydrogen fluoride, is essentially a source of anhydrous nitric acid. Such solutions have been employed successfully for the nitration of a wide variety of aromatic substances (for example, phenols, nitrobenzene, anthraquinone, acetanilide). Pyridine cannot be nitrated in this manner.

It is noteworthy that amines, which ordinarily require protection of the amino groups, may be nitrated directly by dissolving their nitrates in liquid hydrogen fluoride at 0°C. Such reactions can also be effected in heterogeneous systems, thus permitting the nitration of hydrocarbons which have limited solubility in liquid hydrogen fluoride.

Sulfonation reactions can be carried out by methods similar to those employed for nitrations using either concentrated sulfuric acid or potassium sulfate in liquid hydrogen fluoride. Such reactions must, however, be carried out at higher temperatures than those required for nitrations. Moreover, a secondary reaction yielding sulfone often occurs, the ratio of sulfonic acid to sulfone in the product being dependent on the temperature. Thus, sulfonation of benzene with concentrated sulfuric acid at 85° to 90°C. yields 75% benzene sulfonic acid and less than 1% diphenylsulfone; at 140° to 150°C. a 40% yield of the sulfone is obtained. The objections raised to the use of absolute nitric acid for nitrations in liquid hydrogen fluoride apply also to

sulfuric acid. The latter reacts violently with hydrogen fluoride to form fluosulfonic acid, FSO_3H , which, presumably, is the active sulfonating agent. Fluosulfonic acid is more conveniently obtained in hydrogen fluoride by the dissolution of potassium sulfate.*

Unsymmetrical sulfones have been prepared in hydrogen fluoride solution by reaction between a hydrocarbon and either a sulfonyl chloride or a sulfonic acid. The following sequence of reactions undoubtedly occurs in the former instance:



MOLECULAR REARRANGEMENTS. A number of rearrangements or exchange reactions which are commonly catalyzed by other reagents may be effected with liquid hydrogen fluoride. For example, it has been shown that the exchange of alkyl groups by two aromatic compounds and the Beckmann and Fries rearrangements are promoted by this solvent.

Phenol reacts with *tert*-butylbenzene in hydrogen fluoride at 0°C . to give benzene and *tert*-butylphenol, the latter in about 10% yield. No attempt was made to carry out the reaction at higher temperatures although it is probable that the reaction would have been more successful.

The Beckmann rearrangement, involving the conversion of a ketoxime to an anilide, has been carried out at 0°C . in an acetic acid-hydrogen fluoride mixture, and also in an ether-hydrogen fluoride mixture. Thus benzophenone oxime is converted with 72% yield to benzanilide.

Although the Fries rearrangement of phenyl acetate does not take place in pentane-hydrogen fluoride solution at room temperature, *p*-hydroxyacetophenone is obtained in 33% yield when the reaction is carried out at 100°C . under pressure. In liquid hydrogen fluoride the rearrangement of phenyl acetate may be effected at 0°C . A number of phenyl esters have been shown to undergo the Fries rearrangement with good yield when they are refluxed in liquid hydrogen fluoride at about 25°C . In this manner, phenyl acetate yields 92% *p*-hydroxyacetophenone, phenyl benzoate 95% *p*-hydroxybenzophenone, and phenyl salicylate 40% 2,4-dihydroxybenzophenone.

OXIDATION REACTIONS. Simons and McArthur (37) have investigated the oxidation of some aromatic, alicyclic, and aliphatic com-

* Attention is called to the fact that fluosulfonic acid is readily prepared by the direct combination of sulfur trioxide with hydrogen fluoride.

pounds in the liquid phase with molecular oxygen under pressure, in hydrogen fluoride as solvent. The reactions were carried out in a copper bomb under a variety of conditions of temperature ($<200^{\circ}\text{C}.$) and pressure, and in the presence of a number of carriers (for example, Ag_2O , As_2O_3 , As_2O_5 , Fe_2O_3 , SeO_2 , and MoO_3). The products formed in these reactions are not those ordinarily obtained in either the liquid- or the vapor-phase oxidation of the same substances; no tars are formed.

The oxidation of benzene in the presence of oxygen carriers results in the formation of phenol and carbon; carbon monoxide and carbon dioxide are formed only when no carriers are used. Although the ratio of phenol to benzene never exceeded a small value, the yields of phenol, based upon the total amount of carbon compounds other than benzene found in the products, were occasionally quantitative. In some instances small quantities of diphenyl and benzoic acid were also identified as products of reaction. The oxidation of toluene gives chiefly *o*-cresol and carbon, along with minor amounts of benzoic acid and some hydrocarbon material of the nature of bi- and polytolyl mixtures. As is the case with benzene, no formation of ring-rupture products and their oxidized fragments occurs. The oxidation of *m*-xylene gives 1,3-xylene-4-ol, some toluic acid, and carbon. Naphthalene yields β -naphthol, a trinaphthyl, and large quantities of carbon.

The only products obtained from the oxidation of cyclohexane, methylcyclohexane, and *n*-heptane are carbon and water. These compounds apparently are more resistant to oxidation than are the aromatics, a higher temperature being necessary to bring about reaction.

The carbon obtained in all the experiments is in an activated form. When sufficient oxygen is used, all the organic compounds may be converted to carbon without the formation of either carbon monoxide or carbon dioxide.

THE PRODUCTION OF FLUORINE-CONTAINING COMPOUNDS BY ELECTROCHEMICAL MEANS. Of considerable potential value is a process for the manufacture of fluorocarbons and other fluorine-containing compounds by an electrochemical technique (38, 39). The process involves the electrolysis for a period of hours of a liquid hydrogen fluoride solution containing a fluorinatable organic compound. The potential of the cell is maintained at a value which is insufficient to generate elementary fluorine. Where the organic starting compound is insoluble (for example, alkanes), soluble organic (pyridine, diethyl ether, etc.) and inorganic (soluble fluorides, small quantity of water) conductivity additives are provided to permit electrolysis. The cell container and cathode employed are made of steel and iron and the anode of nickel.

The completely fluorinated products, as well as those not completely fluorinated, are relatively insoluble in hydrogen fluoride and either evolve with the cell gases or settle to the bottom of the cell. The formation of the fluorinated compounds involves an anodic process; hydrogen is liberated at the cathode. The reaction mechanism does not involve the formation of elementary fluorine.

Among the products obtainable are those having the same number of carbon atoms and the same carbon skeletal structure as do the starting compounds, but with partial or complete fluorine replacement of hydrogen atoms and other atoms or radicals bonded to the carbon skeleton of the molecule. Fluorine addition occurs with unsaturated and aromatic starting materials to produce saturated products. Non-cyclic compounds (in addition to the expected cyclic ones) having the same number of carbon atoms are produced from cyclic starting compounds as a result of bond cleavage and fluorine addition. Products having fewer carbon atoms in the molecule are obtainable from polycarbon cyclic and non-cyclic starting materials due to fragmentation of the carbon skeleton and fluorine addition. Compounds having a greater number of carbon atoms than the original materials are also obtainable as a result of the coupling of carbon radicals formed in solution. In general, the kinds and relative proportions of products which are produced depend upon the nature of the starting compound and operating conditions.

The versatility of the electrochemical process is demonstrated by the following illustrations. Among the types of compounds which have been obtained in good yield are the following (R represents saturated fluorocarbon radicals):

- $R'OR''$ from ethers.
- $R'R''R'''N$ from tertiary amines.
- $R'R''NF$ from secondary amines.
- RNF_2 from primary amines.
- $RCOF$ from monocarboxylic acids.
- $R'COOR''$ from esters.
- RCN from nitriles.
- RSF from mercaptans.

In addition to the types listed above, a wide variety of other classes of compounds has been prepared. Fluorocarbons which contain combined chlorine can be formed from chlorine-containing compounds (for example, chloroacetic acid). Heterocyclics containing one or more oxygen or nitrogen atoms in the ring are obtainable from compounds of corresponding structure by replacement of hydrogen with

fluorine. True fluorocarbons (compounds containing only carbon and fluorine atoms) are produced either directly from hydrocarbons or by the electrolysis of solutions of various hydrocarbon derivatives (for example, alcohols, monocarboxylic acids). The fluorocarbons thus formed may possess the same number, fewer, or a greater number of carbon atoms than the original starting material. True fluorocarbons having fewer carbon atoms than the starting compound can also be prepared from hetero compounds in which the carbon atoms are linked to such atoms as oxygen or nitrogen.

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LIQUID SULFUR DIOXIDE

The potentialities of liquid sulfur dioxide as a solvent for chemical reactions were first realized by Walden (1) at the turn of the century. At that time, this versatile investigator began a study of the solubility of inorganic and organic substances in this medium and of the electrochemical nature of such solutions. From these initial investigations the chemistry of liquid sulfur dioxide has developed to a status almost comparable to that possessed by liquid ammonia chemistry.

Liquid sulfur dioxide, because of its large-scale industrial use as a refrigerant and as a selective solvent in petroleum refining, is readily available to the chemist. Industrially, the easily liquefiable gas is produced by the roasting of sulfur or metal sulfides. The tank sulfur dioxide of commerce contains 0.005 to 0.1% of water and small amounts of sulfur trioxide as impurities and is readily purified for research purposes. Passage of the gas through concentrated sulfuric acid solution removes sulfur trioxide and most of the water; removal of the last traces of the water may then be accomplished by permitting the gas to pass over phosphoric anhydride. After such treatment, the pure gas may be condensed in the appropriate vessel of the experimental set-up in order to avoid exposure to atmospheric moisture. When a small amount of very pure material is desired, it is frequently obtained by the dropwise addition of chemically pure sulfuric acid to sodium sulfite of high purity. The criterion commonly applied for the estimation of purity is the freezing point of the material, a value in the neighborhood of -72.5°C . being indicative of a high order of purity.

Because of its toxic physiological properties, extreme care must be observed in handling sulfur dioxide. Concentrations as low as 0.04% in the atmosphere will cause symptoms of poisoning in the human being within a few hours; breathing of large quantities frequently may be fatal.

The physical properties of anhydrous sulfur dioxide (Table 62) offer some interesting information with regard to its solvent potentialities.

TABLE 62

SOME PHYSICAL CONSTANTS OF ANHYDROUS SULFUR DIOXIDE (2)

<i>Property</i>	<i>Value</i>
Freezing point, °C.	-72.7
Boiling point, °C.	-10.2
Specific conductivity, ohm ⁻¹	4×10^{-8} (-10°C.)
Specific gravity	1.46 (-10°C.)
Dielectric constant	12.35 (22°C.)
Vapor pressure	{ 1163 mm. (0°C.) 3.228 atm. (20°C.) (3)
Viscosity, poise	0.004285 (-10°C.)

ties. Although its boiling point (-10.2°C.) is quite low, sulfur dioxide can be handled readily in insulated containers, such as Dewar flasks, without excessive losses by evaporation, or in closed containers at room temperature at a few atmospheres pressure. The value for the specific conductance, 4×10^{-8} ohm⁻¹ indicates a self-ionization of the same order of magnitude as that of water. As suggested by its relatively low dielectric constant, sulfur dioxide should dissolve covalent compounds to a markedly greater extent than ionic substances; interionic effects should be large in solutions of ionic substances.

SOLVENT PROPERTIES

SOLUBILITY OF INORGANIC SUBSTANCES. As a result of the investigations of Walden and Centnerszwer (1, 4), Jander and co-workers (5, 6, 7), Shatenshtein and Viktorov (8), and Bond and co-workers (9), considerable data regarding the solubility of inorganic substances in liquid sulfur dioxide have been accumulated. In general, covalent substances are usually considerably more soluble than ionic compounds. For example, bromine, boron trichloride, carbon disulfide, phosphorus(III) chloride, phosphorus(V) oxychloride, arsenic(III) chloride, iodine monochloride, and the various thionyl compounds are miscible with the solvent in all proportions; iodine monobromide, phosphorus(III) bromide, and the group IV tetrahalides are quite soluble. Alkali metal and ammonium iodides and thiocyanates are among the most soluble of the inorganic salts. It is interesting to note that the iodides exhibit a negative temperature coefficient of solubility. As is usually the case in non-aqueous solvents, the solubility of the alkali metal halides decreases in the order $I^- > Br^- > Cl^-$. The behavior of the silver halides in sulfur dioxide is directly contrary to that in water, the solubility decreasing in the order $I^- > Br^- > Cl^- > F^-$.

Metal oxides, sulfates, sulfides, and hydroxides are practically insoluble; the solubility of nitrates cannot be determined since they appear to react with the solvent. Quantitative solubility data available for inorganic salts are summarized in Table 63.

TABLE 63

MAXIMUM SOLUBILITIES OF INORGANIC SALTS IN SULFUR DIOXIDE AT 0°C.
IN MILLIMOLES PER 1000 G. SO₂ (6)

Ion	SO ₃ ⁼	F ⁻	Cl ⁻	Br ⁻	I ⁻	SCN ⁻	CN ⁻	ClO ₄ ⁻	CH ₃ COO ⁻	SO ₄ ⁼	CO ₃ ⁼
Li ⁺		23.0	2.82	6.0	1490.0				3.48	1.55	
Na ⁺	1.37	6.9	insol.	1.36	1000.0	80.5	3.67		8.90	insol.	
K ⁺	1.58	3.1	5.5	40.0	2490.0	502.0	2.62		0.61	insol.	
Rb ⁺	1.27		27.2								
NH ₄ ⁺	2.67		1.67	6.0	580.0	6160.0		2.14	141.0	5.07	
Tl ⁺	4.96	insol.	0.292	0.60	1.81	0.915	0.522	0.43	285.0	0.417	0.214
Ag ⁺	insol.	insol.	<0.07	0.159	0.68	0.845	1.42		1.02	insol.	
Be ⁺⁺			5.8								
Mg ⁺⁺	insol.		1.47	1.3	0.50						
Ba ⁺⁺			insol.	insol.	18.15	insol.					
Zn ⁺⁺			11.75		3.45	40.4			insol.		
Cd ⁺⁺			insol.		1.17						
Hg ⁺⁺			3.80	2.06	0.265	0.632	0.556		2.98	0.338	
Pb ⁺⁺		2.16	0.69	0.328	0.195	0.371	0.386		2.46	insol.	
Co ⁺⁺			1.00		12.2	insol.					
Al ⁺³			very sol.	0.60	5.64						
Sb ⁺³		0.56	575.0	21.8	0.26						
Bi ⁺³			0.60	3.44							
Ni ⁺⁺			insol.		insol.				0.03	insol.	insol.

In liquid sulfur dioxide, as in other solvents, the extent of solubility of salts appears, qualitatively, to go hand in hand with the tendency toward solvate formation. It is true, however, as has been pointed out by Jander and Mesech (10) in their excellent review of the general topic of solvated salts in liquid sulfur dioxide, that solvate formation is not confined solely to readily soluble salts. Such considerations as the temperature coefficient of solubility and lattice energy of the solvate are of considerable importance in determining the tendency toward solvate formation. Nevertheless, the more soluble salts form the most stable solvates. With few exceptions, these solvates are limited to salts containing alkali or alkaline earth metals

and the ammonium or substituted ammonium radicals as cations, and iodide, thiocyanate, bromide, chloride, or fatty acid radicals as anions.

SOLUBILITY OF ORGANIC SUBSTANCES. The pioneer work of Walden (1) demonstrated that, with few exceptions, liquid sulfur dioxide is an excellent solvent for organic substances. Amines, esters, alcohols, phenols, acids, and aromatic hydrocarbons and their derivatives are readily soluble; however, saturated aliphatic compounds possess only limited solubility. This marked difference in solubility between the paraffin and aromatic hydrocarbons has proved to be of some industrial importance. It was first utilized by Edeleanu (11) for the refining of kerosene which was to be used for illuminating purposes. Extraction of the crude kerosene with liquid sulfur dioxide removes aromatic hydrocarbons and sulfur-containing materials which are responsible for a smoky flame, carbonization of the wick, and the instability of the color of the flame. From the modest beginning just cited, the Edeleanu process has been expanded to a stage where it is of considerable utility in the refining of petroleum products (12). A brief discussion of some significant factors involved in its use for this purpose is given below.*

Solubility studies (12, 13, 14, 15) on the various components of petroleum mixtures have revealed the following important facts. Olefins, aromatic hydrocarbons, organic sulfides, disulfides, and mercaptans are completely miscible with liquid sulfur dioxide. Amorphous sulfur, nitrogen compounds, and asphalt-like compounds are readily soluble. The solubility of paraffin hydrocarbons decreases with increasing molecular weight, and at low temperatures (about $-10^{\circ}\text{C}.$) the solubility of even the lower members of the paraffin series is quite limited. Naphthenes are somewhat more soluble than paraffin hydrocarbons, but not to a sufficient degree to permit practical separation of the two types. It is apparent that the presence of such a wide variety of substances involves complicated solubility relationships, and, therefore, a sharp separation cannot be obtained. A satisfactory separation for refining purposes can, nevertheless, frequently be achieved.

The usefulness and limitations of liquid sulfur dioxide as an extractive solvent become apparent from a consideration of the specifications of a few petroleum products. The prime requirements of gasoline are high octane rating, low sludge formation, and low sulfur content. Obviously, the low temperature extraction of a gasoline of low octane rat-

* For a thorough discussion of the use of liquid sulfur dioxide for the refining of petroleum products, see Kalichevsky and Stagner, *Chemical Refining of Petroleum*, Reinhold Publishing Corporation, New York, 1942.

8. Compounds of the following types: $\text{CH}_3\text{OC}_6\text{H}_4\text{CCl}_2\text{C}_6\text{H}_4\text{OCH}_3$, $\text{CH}_3\text{OC}_6\text{H}_4\text{CHClCH}=\text{CClC}_6\text{H}_4\text{OCH}_3$, and $\text{CH}_3\text{OC}_6\text{H}_4\text{CHClCH}=\text{CClCH}=\text{CHC}_6\text{H}_4\text{OCH}_3$.

Some of the organic compounds which act as "abnormal" electrolytes give solutions which exhibit a conductivity of the same order of magnitude as that of true binary salts. This is illustrated by the data presented in Table 64.

TABLE 64

EQUIVALENT CONDUCTANCE OF SOME ELECTROLYTES IN LIQUID SULFUR DIOXIDE

($t = 0^\circ\text{C}.$; $V = 1024$ liters/mole)

Compound	Λ , ohm^{-1}
KI	112.4
$[(\text{C}_2\text{H}_5)_4\text{N}]\text{I}$	164.8
$[(\text{CH}_3)_4\text{N}]\text{Br}$	158.8
$(\text{C}_6\text{H}_5)_3\text{CBr}$	153
$(\text{C}_6\text{H}_5\text{C}_6\text{H}_4)_3\text{CCl}$	121
$ \begin{array}{c} \text{CH}_3\text{OC}_6\text{H}_4 \quad \text{Cl} \\ \quad \diagdown \quad \diagup \\ \quad \text{C} \\ \quad \diagup \quad \diagdown \\ \text{CH}_3\text{OC}_6\text{H}_4 \quad \text{Cl} \end{array} $	130

Jander and Mesech (17) have studied the effect of concentration on the conductivity of many salts and have shown that the conductivity versus concentration curves exhibit two minima. This phenomenon, which had previously been observed by Franklin (18), is frequently encountered in solvents of low dielectric constant. The re-

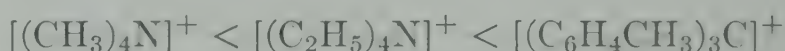
TABLE 65

THE MOLAR CONDUCTIVITY OF POTASSIUM IODIDE IN VARIOUS SOLVENTS

Dilution, liters/mole	Water, $25^\circ\text{C}.$	Ammonia, $-33.5^\circ\text{C}.$	Sulfur Dioxide, $-10^\circ\text{C}.$
1	46.9
2	(136)	46.8
5	147	44.0
10	130.8	152	42.6
20	134.7	161	44.6
50	139.4	184	52.4
100	142.3	216	61.8
200	144.5	231	75.4
500	146.7	...	98.4
1000	147.9	...	118.8
∞		332	222.0

sults of the studies of Jander and Mesech demonstrate the large magnitude of interionic effects in liquid sulfur dioxide. (The conductivity data of potassium iodide in Table 65 emphasize this point.) It was found that the limiting conductance of sulfur dioxide solutions can be approached at very high dilutions, and that both the Ostwald dilution law and the law of independent mobility of ions are valid for "strong" electrolytes at high dilutions.

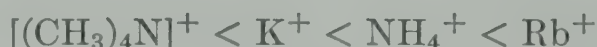
The order of increasing dissociation and conductivity of salts appears to parallel the order of increasing cationic size:



However, a similar relationship does not hold with regard to anion size, probably because of solvation effects. For salts of a common cation, the following order exists:



The mobilities of various ions studied may be arranged in the following sequences:



Jander and Mesech (19) have also measured the mole numbers (that is, the van't Hoff *i* factor) of a wide variety of solutes in liquid sulfur dioxide by the ebullioscopic method. For all non-electrolytes the mole number is one, within the limits of experimental error. Thionyl compounds (for example, SOCl_2) are weak electrolytes in

TABLE 66

MOLE NUMBERS OF SOME UNI-UNIVALENT ELECTROLYTES IN LIQUID SULFUR DIOXIDE

($V = 16$ liters/mole)

<i>Electrolyte</i>	<i>Mole Number</i>
KSCN	0.78
KBr	0.95
KI	1.08
K(SbCl ₆)	1.36
$[(\text{CH}_3)_4\text{N}]\text{Cl}$	1.06
$[(\text{CH}_3)_4\text{N}]\text{ClO}_4$	1.26
$[(\text{C}_6\text{H}_5)_3\text{C}]\text{Cl}$	1.30

liquid sulfur dioxide and also have mole numbers of one. In concentrated solutions, uni-univalent electrolytes give mole numbers which indicate large effects of ion-association of some type (Table 66). In very dilute solutions the mole numbers of these electrolytes approach two. This behavior is concordant with the results obtained in conductivity studies (17).

The salt-like character of certain tertiary oxonium compounds has been demonstrated by the magnitude of their conductivities in liquid sulfur dioxide (20). Pertinent data are given in Table 67.

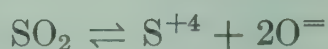
TABLE 67

EQUIVALENT CONDUCTANCE OF SOME TERTIARY OXONIUM SALTS IN LIQUID SULFUR DIOXIDE

<i>Salt</i>	<i>Dilution</i> (liters/mole)	Λ , ohm ⁻¹
[(C ₂ H ₅) ₃ O](BF ₄)	497	112
[(CH ₃) ₃ O](BF ₄)	688	100.2
[(C ₂ H ₅) ₃ O](SbCl ₆)	644	108
[(C ₂ H ₅) ₃ S](BF ₄)	661	124

REACTIONS IN LIQUID SULFUR DIOXIDE

ELECTROLYSES. Additional information regarding the electrochemical nature of sulfur dioxide solutions has been obtained from studies of the behavior of such solutions under the influence of the electric current. The nature of the cathode product in the electrolysis of salts has been the subject of conflicting reports. Steele (21) and Bagster and Steele (22) have claimed that sulfur is obtained as a cathode product during the electrolysis of potassium or sodium iodide between a variety of electrodes. These results were offered in support of the mechanism of self-ionization of sulfur dioxide postulated by Walden (23):



However, the observations of Centnerszwer and Drucker (24) are not in agreement with those of Bagster and Steele. These investigators found no free sulfur at the cathode, but rather a deposit of strongly reducing properties, rich in combined sulfur. This has been confirmed for a variety of salts by Cady and Taft (2), who believe that the deposition of cathodic sulfur may be attributed to the presence of traces of dissolved water in the solutions. All investigators, however,

are in agreement that anodic processes in liquid sulfur dioxide are in general similar to those in water for the same substances.

Bruner and Bekier (25) have studied the electrolysis of bromine, iodine monobromide, and iodine trichloride, so-called abnormal electrolytes, in liquid sulfur dioxide. When a solution of bromine in anhydrous sulfur dioxide is electrolyzed at -20°C ., one equivalent of the halogen is deposited at a silver anode for each faraday of electricity which passes through the solution. Long electrolysis of iodine monobromide solution at 220 volts results in the deposition of 94% of the solute at the anode, as a mixture of the silver halides. In one experiment, of relatively short duration, only silver bromide was found at the anode. In no instance was iodine deposited at the cathode. Electrolysis of iodine trichloride yields only silver chloride at the anode. As in the previous case, no evidence for the formation of elementary iodine is obtained. Although the cathodic processes have not been elucidated, there appears to be no doubt but that they involve participation of the positive entity formed by the self-ionization of the solvent.

Evidence for the existence of the hydronium ion, H_3O^+ , has been obtained from experiments involving the electrolysis of a mixture of water and hydrogen bromide in liquid sulfur dioxide (26). Although neither water nor hydrogen bromide is a conductor in sulfur dioxide, a mixture of the two gives a conducting solution. Electrolysis of such a mixture results in the liberation of bromine at the anode and water and hydrogen at the cathode. Solubility measurements show that water dissolves in liquid sulfur dioxide in equimolecular proportion to the quantity of hydrogen bromide present. In addition, the quantity of water deposited at the cathode is in good agreement with that calculated on the basis of Faraday's law for the reduction of a particle of the formula H_3O^+ . The volume of hydrogen liberated, however, is less than the theoretical quantity.

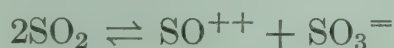
Reference has already been made to the fact that certain tertiary alkyl halides give conducting solutions in liquid sulfur dioxide (16). It is possible to prepare the corresponding free radicals by the electrolysis of such solutions. For example, triphenylmethyl has been obtained at the cathode upon the electrolysis of a sulfur dioxide solution of triphenylmethyl bromide between platinum electrodes (27).

THE "SULFITO" CHEMICAL SYSTEM. Present knowledge of the nature of inorganic chemical reactions in liquid sulfur dioxide is primarily the result of the fundamental investigations of Jander and his collabo-

rators. The foundation for the "sulfito" chemical system was laid by Jander and Wickert (28) in an attempt to place the chemistry of liquid sulfur dioxide on the same footing as the chemistry of water and liquid ammonia. These investigators utilized the hypotheses first propounded by Cady and Elsey (29) regarding the mechanism of self-ionization of liquid sulfur dioxide and the relationship between this mechanism and acid-base behavior in the solvent. Sulfur dioxide is assumed to dissociate in the following manner:



or



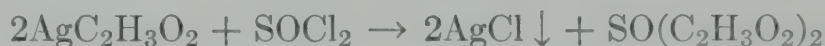
This dissociation is analogous to corresponding reactions for water and liquid ammonia:



On the basis of the proposed mechanism of self-ionization, compounds, such as the thionyl derivatives, potential sources of SO^{++} ions, can be regarded as acid analogs in liquid sulfur dioxide, whereas substances possessing the $\text{SO}_3^=$ ion can be considered to be bases or base analogs. If the analogy to water and liquid ammonia is to hold, one should expect the following characteristic types of reactions to take place in liquid sulfur dioxide: (a) solvate formation; (b) metathesis; (c) neutralization; (d) solvolysis; (e) reactions depicting amphoteric behavior; (f) oxidation-reduction; and (g) complex compound formation. Mention has already been made of solvate formation in liquid sulfur dioxide. The remaining types of reactions have also been shown to take place. The survey of them which follows demonstrates that the concept of a "sulfito" chemical system rests on a firm foundation. Certainly, this useful concept has stimulated much research in liquid sulfur dioxide.

METATHETICAL REACTIONS (OTHER THAN NEUTRALIZATIONS). Walden (1) first demonstrated that metathetical reactions can occur in liquid sulfur dioxide. He showed that reaction between potassium iodide and trimethylamine hydrochloride results in the precipitation of potassium chloride and the formation of the hydroiodide of the amine.

Interesting double decomposition reactions involving thionyl compounds have been reported by Jander and his co-workers. A suspension of silver acetate in liquid sulfur dioxide reacts with thionyl chloride to give a precipitate of silver chloride and a solution of thionyl acetate (7):



Attempts to isolate thionyl acetate proved unsuccessful, since it decomposes readily to sulfur dioxide and acetic anhydride. Reaction between ammonium thiocyanate and thionyl chloride at -18°C . results in the precipitation of the ammonium halide, leaving a solution of the thionyl derivative, $\text{SO}(\text{SCN})_2$ (30). When the solution is cooled to -80°C ., crystals appear which resemble manganese(II) sulfate in color. When warmed to -10°C ., however, the thiocyanate decomposes and an orange-colored material, presumably related to polymeric thiocyanogen, $(\text{SCN})_x$, is formed. The addition of thionyl chloride to a solution of potassium iodide yields potassium chloride, as expected, but no thionyl iodide (30). Instead elementary iodine and sulfur are formed, presumably as a result of the following sequence of reactions:



The reaction between thionyl chloride and potassium bromide has been followed conductometrically (Figure 25) (7). Examination of Figure 25 indicates that the initial metathetic reaction is followed by the formation of a complex of the composition $\text{SOBr}_2 \cdot 2\text{KBr}$.

A potentially useful metathesis involves reaction between potassium iodide and hydrogen chloride to give potassium chloride and a solution of hydrogen iodide (7). This double decomposition offers a convenient method for preparing anhydrous hydrogen iodide in a relatively inert solvent and is favored by the relatively low solubility of potassium chloride as compared to that of potassium iodide.

NEUTRALIZATION REACTIONS. It has been pointed out that thionyl compounds, potential sources of SO^{++} ions, and sulfites, which yield the SO_3^- ion in solution, may be regarded as acids and bases, respectively, in liquid sulfur dioxide. A typical neutralization reaction in sulfur dioxide should, therefore, involve the combination of the acidic thionyl ion with the basic sulfite ion to give solvent molecules:



That such reactions can take place was first demonstrated by Puffett (31), who obtained cesium chloride as a result of reaction between thionyl chloride and cesium sulfite.

Considerable additional experimental evidence for such neutralization reactions has been obtained by Jander and co-workers (7, 30) with a variety of thionyl compounds and sulfites. These investigators followed conductometrically the course of such reactions and also isolated and identified the various products. The reaction between

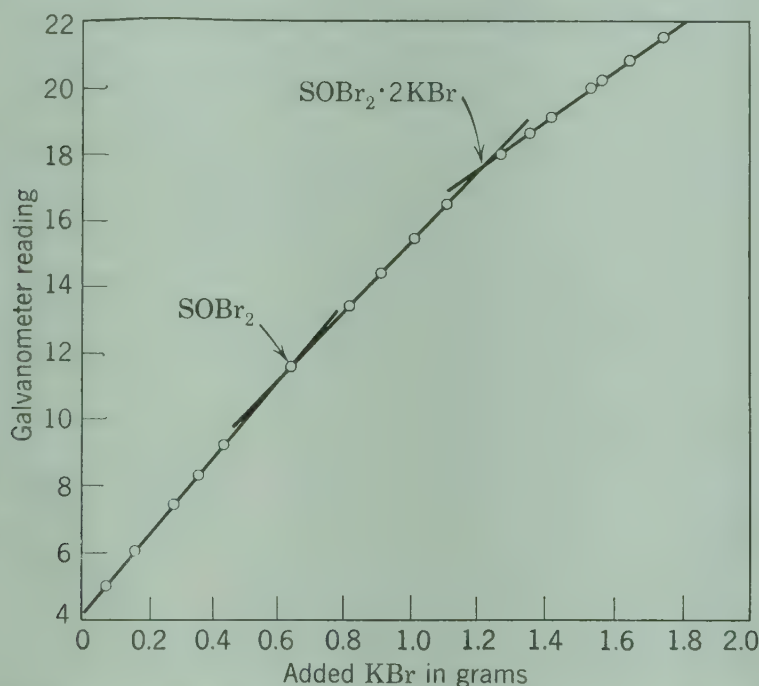


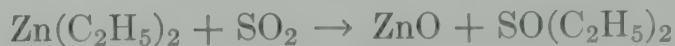
FIGURE 25. Conductometric titration of SOCl_2 with KBr in liquid sulfur dioxide.

tetramethylammonium sulfite and thionyl chloride is particularly interesting. The course of the reaction is depicted in Figure 26. It is postulated that the first break in the conductance curve corresponds to the formation of an acid salt, which unfortunately could not be isolated.

The acid nature of thionyl chloride in liquid sulfur dioxide is further demonstrated by the fact that it reacts with metallic iron at room temperature to give iron(II) chloride and free sulfur. The latter substance undoubtedly comes from the disproportionation of the thionyl radical, SO , which is an intermediate in the reaction.

SOLVOLYTIC REACTIONS. In view of the fact that most of the salts which react with liquid sulfur dioxide do so only slowly, sometimes even under rather severe conditions, solvolytic reactions in this solvent are of only secondary importance. Nevertheless, they present sufficient points of interest to warrant consideration. The first re-

ported case of a solvolytic reaction involves the organometallic compound, diethyl zinc (32). This substance reacts with liquid sulfur dioxide, even at the temperature of an ether and Dry Ice bath, to yield diethyl sulfoxide and a compound which is presumably zinc oxide:



The solvolytic action of liquid sulfur dioxide on various inorganic compounds has also been investigated (33). Alkali metal iodides and

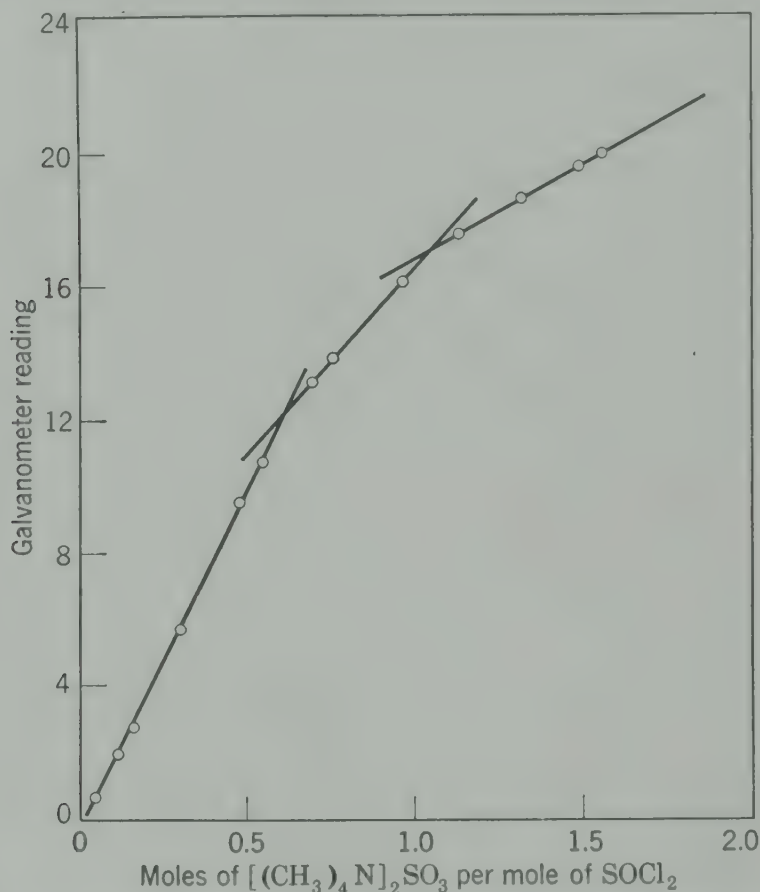
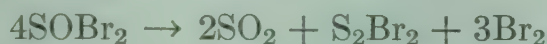


FIGURE 26. Conductometric titration of $[(\text{CH}_3)_4\text{N}]_2\text{SO}_3$ with SOCl_2 in liquid sulfur dioxide.

bromides react slowly with liquid sulfur dioxide in a sealed tube at room temperature. On long standing a crystalline precipitate is obtained which is shown by analysis to be an equimolecular mixture of potassium sulfate and sulfur when potassium iodide is employed; only potassium sulfate is obtained when the bromide is used. In the former instance, elementary iodine is found in solution, whereas, in the latter, bromine and sulfur monobromide are identified in solution. The probable mechanism of the reaction is illustrated here for potassium bromide:



The rate of solvolysis of the alkali metal halides is markedly increased with increasing dilution of the salt.

Heating the mixture of potassium iodide and sulfur dioxide at 100°C. has relatively little effect on the quantity of potassium sulfate formed, since the temperature coefficient of solubility of potassium iodide is strongly negative. For the same reason, potassium bromide is recovered unchanged when kept in contact with liquid sulfur dioxide at 100°C. for several days. It is interesting that both lithium iodide and bromide are rapidly solvolyzed even at -30°C. This is explained by the fact that the salt is derived from lithium sulfite, which is a considerably weaker base analog than potassium sulfite.

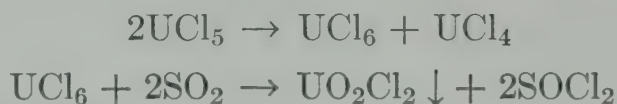
Alkali metal acetates are slowly solvolyzed in sulfur dioxide even at -50°C. The reaction is a difficult one to follow, since both the acetate and the product of solvolysis (metal sulfite) possess relatively limited solubility. At 70° to 80°C., in a sealed tube, the extent of solvolysis is increased considerably. In fact, it has been suggested that reaction of the acetates under these conditions might serve as a useful method for the preparation of anhydrous, sulfate-free sulfites. In addition to metal sulfite, acetic anhydride, presumably resulting from the decomposition of the intermediate thionyl acetate, is identified as a solvolytic product. The solvolytic behavior of aluminum acetate has also been studied. At 90°C., about 50% conversion to the sulfite occurs after several days.

The behavior of the halides of groups IV, V, and VI of the short form of the periodic classification toward attack by liquid sulfur dioxide is variable, and no generalizations can be drawn. Silicon(IV) and tin(IV) chlorides do not react, even when heated for some time in a bomb at 90° to 100°C. The solvolytic reaction for the halides of group V appears to be dependent on the metallic character of the element bound to the halogen. Phosphorus(V) chloride is readily attacked, even at -50°C., in the following manner:



Antimony(III) and (V) chlorides are recovered unchanged after treatment for 12 hours at 60° to 70°C. in a sealed tube. Vana-

dium(IV) chloride is unattacked by liquid sulfur dioxide at room temperature. At 60° to 70°C., however, it is thermally decomposed, with the liberation of chlorine and the precipitation of violet needles of the trichloride. Solutions of niobium(V) chloride become cloudy after standing for several days at room temperature. At 70°C., the solvolytic process is considerably accelerated, with the result that crystals of niobium(V) oxychloride, NbOCl_3 , appear after several hours. On the other hand, tantalum(V) chloride and bromide, which are but slightly soluble in liquid sulfur dioxide, do not undergo solvolysis. Of the various halides of group VI which have been studied, for example, SCl_2 , SCl_4 , MoCl_5 , WCl_6 , and UCl_5 , only the last two react with the solvent. A solution of tungsten(VI) chloride, which has been kept for a short time at 60° to 70°C. yields, on cooling, red needles of the pure oxychloride, WOCl_4 , a substance which is difficult to prepare by other means. Although the reaction between uranium(V) chloride and liquid sulfur dioxide has not been completely elucidated, it appears probable that at 80° to 90°C. it proceeds in the following manner:



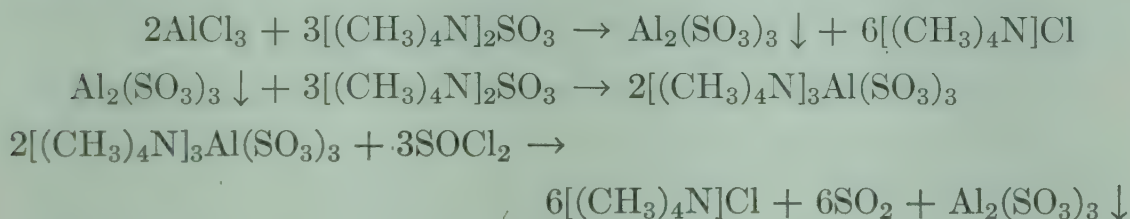
Anilinium salts react in a characteristic solvolytic fashion in liquid sulfur dioxide, with the formation either of a more highly acid salt or of the free acid (33).



Thus, difficultly soluble, neutral anilinium oxalate, $(\text{C}_6\text{H}_5\text{NH}_2 \cdot \text{H})_2(\text{COO})_2$, is converted to the acid salt, $(\text{C}_6\text{H}_5\text{NH}_2 \cdot \text{H})[\text{H}(\text{COO})_2]$; the acid anilinium succinate, $(\text{C}_6\text{H}_5\text{NH}_2 \cdot \text{H})[\text{H}(\text{CH}_2\text{COO})_2]$, gives insoluble succinic acid. The order of increasing tendency toward solvolysis, for the various anilinium salts, parallels that of decreasing strength (in water) of the parent acids. The observed order of solvolysis is: sulfate < oxalate < phosphate < monochloroacetate < succinate.

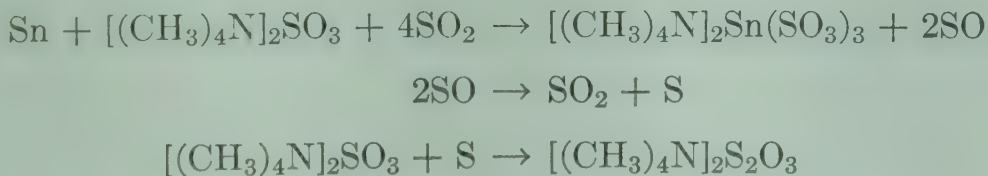
REACTIONS DEPICTING AMPHOTERIC BEHAVIOR. Striking support for the concept of a "sulfito" chemical system is offered in a series of investigations by Jander and collaborators (34, 35, 36) dealing with amphoteric behavior in liquid sulfur dioxide. Aluminum sulfite, $\text{Al}_2(\text{SO}_3)_3$, which may be compared to its aquo analog, aluminum hydroxide, is shown by its reactions with tetramethylammonium sulfite and thionyl chloride, base and acid analogs, respectively, to possess amphoteric characteristics in liquid sulfur dioxide (34). The mixing of solutions of aluminum chloride and tetramethylammonium sulfite

results in the formation of aluminum sulfite as a gelatinous precipitate. This precipitate may be dissolved by rapid treatment with an excess of the base analog; the addition of thionyl chloride to the solution so formed results in the reprecipitation of aluminum sulfite. The aluminum sulfite is not soluble in an excess of thionyl chloride, a fact which is attributed to rapid aging. Conductometric experiments on the sequence of reactions described above indicate that they occur stoichiometrically in accordance with the following equations:



Similar experiments with tin(IV) chloride demonstrate that this substance behaves in a manner analogous to that of aluminum chloride (35). Moreover, conductometric titrations show that the tin(IV) oxide solvate, $\text{SnO}_2 \cdot x\text{SO}_2$, initially precipitated by the addition of tetramethylammonium sulfite, dissolves in an excess of the sulfite to give a solution containing the corresponding orthosulfitostannate, $[(\text{CH}_3)_4\text{N}]_4\text{Sn}(\text{SO}_3)_4$. The solvates of bismuth(III), gallium(III), and antimony(III) and (V) oxides also exhibit amphoteric characteristics in liquid sulfur dioxide.

A property typical of metals whose oxides are amphoteric in the water system is their ability to dissolve in a strong aquo base with the liberation of hydrogen. In an attempt to determine whether an analogous situation prevails in the sulfur dioxide system, the action of the base analog tetramethylammonium sulfite on a variety of metals was studied (35). Beryllium, aluminum, gallium, antimony, and lead, metals whose oxides are amphoteric in the aquo system, give no reaction with tetramethylammonium sulfite in liquid sulfur dioxide. Tin foil, however, does react to give products whose nature depends upon the quantity of base analog used. With an excess of tetramethylammonium sulfite the reaction proceeds according to the following equations:

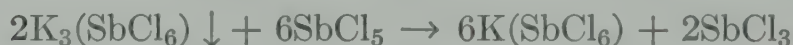


When tin and tetramethylammonium sulfite are brought together in equimolecular proportions, tin(IV) oxide solvate is precipitated.

OXIDATION-REDUCTION REACTIONS. Oxidation-reduction reactions may be carried out in liquid sulfur dioxide. The sulfur dioxide functions merely as the solvent in these reactions, for it has been shown that oxidizing agents, for example, bromine and iodine, may be recovered unchanged from solution in this medium. A few oxidation-reduction reactions which take place in sulfur dioxide are described below.

Tetramethylammonium sulfite is rapidly converted to the sulfate by reaction with iodine (34). A similar, but much slower, oxidation occurs when the less soluble alkali metal sulfites are used.

The oxidation of potassium iodide by antimony(V) chloride proceeds practically quantitatively, as evidenced from the determination of the quantity of elementary iodine liberated (34). Much of the antimony(III) chloride formed by the reduction of the corresponding pentapositive antimony compound is precipitated as a complex of the formula $K_3(SbCl_6)$. A conductometric study of the reaction indicates that this complex may be converted to a similar complex containing +5 antimony upon treatment with an excess of antimony(V) chloride. The following equations describe the stoichiometry of the various reactions as determined conductometrically:



COMPLEX COMPOUND FORMATION. Numerous instances of the formation in liquid sulfur dioxide of complex compounds, other than solvates, are cited in the literature. The first recorded evidence of complex formation in this solvent was the observation of Walden (1) that the characteristic red color of the iron(III) thiocyanate complex is obtained when iron(III) chloride and ammonium thiocyanate are brought together.

Walden and Centnerszwer (4) noticed that added iodine increases the conductivity of such electrolytes as potassium and rubidium iodides in sulfur dioxide, and that the addition of these electrolytes greatly increases the solubility of the iodine. Since a molar ratio of metal iodide to free iodine of 1:1 was necessary for maximum effect, the phenomena described above were attributed to the formation of potassium triiodide, KI_3 . Evidence for the formation of complex iodides of cadmium and mercury(II) is offered by the fact that the solubility of the iodides of these elements is considerably increased by the addition of potassium or rubidium iodide.

The formation of the complexes $K_3(SbCl_6)$ and $K(SbCl_6)$ has already been described in the discussion of the oxidation of potassium

iodide by antimony(V) chloride. Other hexachloroantimony complex compounds have also been prepared by Jander and co-workers. The conductometric titration of antimony(III) chloride with thionyl chloride (Figure 27) demonstrates the existence of $(\text{SO})_3(\text{SbCl}_6)_2$ (34). Unfortunately this complex proved to be too unstable to be isolated. The compound $[(\text{CH}_3)_4\text{N}](\text{SbCl}_6)$, which has been isolated from a solution containing tetramethylammonium chloride and antimony(V) chloride, appears to be quite stable in solution, since it is not decom-

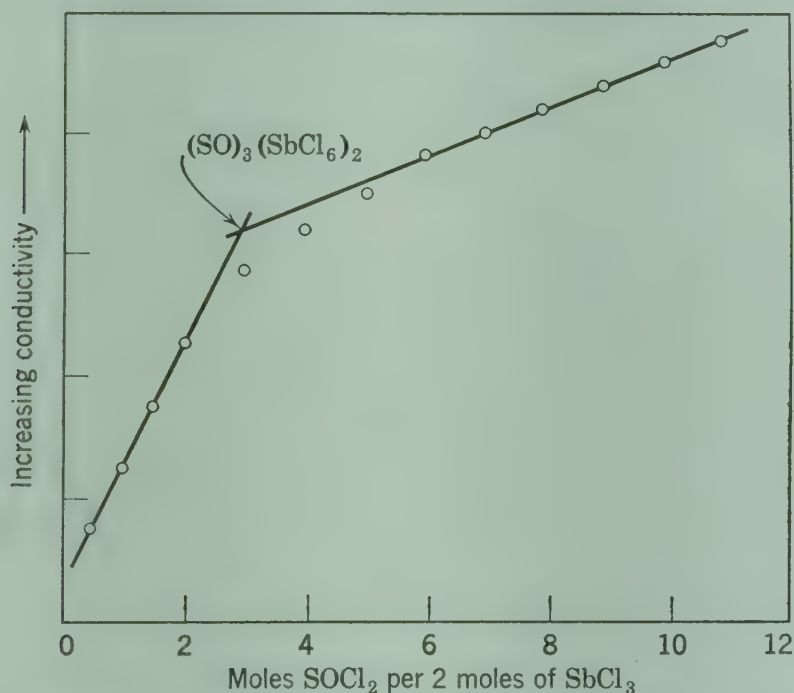
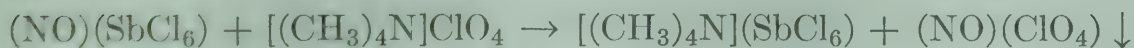


FIGURE 27. Conductometric titration of SbCl_3 with SOCl_2 in liquid sulfur dioxide.

posed by the addition of the base analog tetramethylammonium sulfite (37). Seel (38) has described the preparation and characterization of some unusual complexes containing the hexachloroantimonate(V), $(\text{SbCl}_6)^-$, group. Reaction between nitrosyl chloride and antimony(V) chloride in sulfur dioxide produces a bright yellow solution from which the readily sublimable compound, $(\text{NO})(\text{SbCl}_6)$, may be obtained by evaporation of the solvent. When antimony(V) chloride and acetyl chloride are brought together, a colorless solution of $(\text{CH}_3\text{CO})(\text{SbCl}_6)$ is formed. Metathetical reactions of the following types have been carried out with sulfur dioxide solutions of these complexes:



Antimony(V) chloride and the various acid chlorides which have been used in the preparation of complexes of the type described above are very poor conductors in liquid sulfur dioxide. Most of the complexes themselves, however, on the basis of the conductivity data shown in Table 68, would appear to be salt-like in character (38).

TABLE 68

EQUIVALENT CONDUCTIVITIES OF SOME HEXACHLOROANTIMONATE(V)
COMPLEXES IN LIQUID SULFUR DIOXIDE

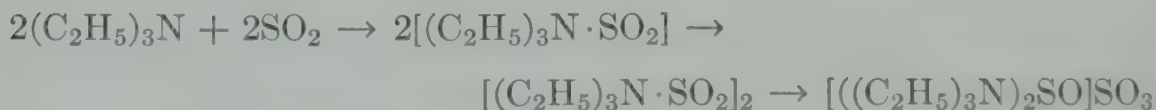
($V = 50$ liters/mole)

<i>Compound</i>	Λ , ohm^{-1}	
	$0^{\circ}C.$	$-70^{\circ}C.$
$K(SbCl_6)$	92.8	49.0
$(CH_3CO)(SbCl_6)$	80.5	45.3
$(C_6H_5CO)(SbCl_6)$	71.5	37.8
$(NO)(SbCl_6)$	67.5	50.0
$(SO)(SbCl_6)_2$	0.4	0.7

Another noteworthy complex compound which has been prepared in liquid sulfur dioxide is acetyl fluoborate, $(CH_3CO)(BF_4)$ (39). It is obtained by the direct combination of acetyl fluoride and boron trifluoride and appears to possess some ionic character. It possesses an equivalent conductance in liquid sulfur dioxide of $12.7\ ohms^{-1}$ at $-70^{\circ}C.$ and a dilution of 79 liters per mole. It exhibits an appreciable boron trifluoride vapor pressure at room temperature, but practically none at $-50^{\circ}C.$ Reaction of acetyl fluoborate with potassium acetate in liquid sulfur dioxide results in the precipitation of potassium fluoborate.

THE JANDER INTERPRETATION OF THE STRUCTURE OF AMINE SOLVATES. The wide variety of reactions which have been shown to take place in liquid sulfur dioxide emphasizes the utility of the "sulfito" chemical system as propounded by Jander. However, the interpretation by Jander of one type of reaction, namely, that between amines and sulfur dioxide, in terms of the "sulfito" system, has been subjected to severe criticism.

According to Jander and his collaborators (7, 34, 40, 41), amines and liquid sulfur dioxide react in the manner depicted below for triethylamine:



The following evidence is offered for the existence of the compound $[((\text{C}_2\text{H}_5)_3\text{N})_2\text{SO}]\text{SO}_2$, which is described as a colorless, crystalline material melting at 73°C ., and which is obtained by evaporation of the solvent (40, 34). This substance gives an electrically conducting solution in liquid sulfur dioxide, a 0.014 molar solution having a specific conductivity of $1.2 \times 10^{-4} \text{ ohm}^{-1}$ at -19°C . Moreover, it presumably undergoes metathesis with potassium bromide in the following fashion:



A conductometric titration of a sulfur dioxide solution of iodine with a solution of triethylamine in toluol is explained on the basis of the following reaction:



Grave doubts of the validity of the interpretation described above have been cast by the work of Bateman, Hughes, and Ingold (42). Working under anhydrous conditions, these investigators have obtained an orange-red liquid upon the dissolution of triethylamine in liquid sulfur dioxide. When this orange-red liquid is cooled to -80°C ., a colorless crystalline solid is obtained which melts below 0°C . to give the original liquid material. The apparent molecular weights of the orange-red liquid and of triethylamine in liquid sulfur dioxide show that a simple molecular compound of the formula $(\text{C}_2\text{H}_5)_3\text{N} \cdot \text{SO}_2$ is formed. In addition, the solution of the amine possesses a small electrical conductivity, indicating that only a small proportion of the solute exists in the form of ions. The orange-red material absorbs water rapidly and oxygen slowly when exposed to the atmosphere. The absorption of water results in the formation of a substance of the formula $(\text{C}_2\text{H}_5)_3\text{N} \cdot \text{SO}_2 \cdot \text{H}_2\text{O}$ [or $(\text{C}_2\text{H}_5)_3\text{NH}(\text{HSO}_3)$], which melts at 74° to 75°C . Bateman, Hughes, and Ingold believe that this is the substance to which Jander has ascribed the formula $[((\text{C}_2\text{H}_5)_3\text{N})_2\text{SO}]\text{SO}_3$.

In the light of the above observations, they believe that claims for the occurrence of metathetical reaction between the amine-solvate and potassium bromide, and also of oxidation of the solvate with iodine, are untenable. Moreover, they point out that identification of $[((\text{C}_2\text{H}_5)_3\text{N})_2\text{SO}]\text{Br}_2$ is based upon an analysis which gives a sulfur content corresponding to an incorrectly calculated theoretical value.

It must be said that there is much additional evidence in the literature to indicate that the degree of ionization of amine-sulfur dioxide

complexes is so slight as to be of little significance in determining the chemical behavior of their solutions.* Finally, although it is true that Jander's interpretation of the structure of amine-sulfur dioxide complexes is open to considerable doubt, this fact in no way invalidates the usefulness of the "sulfito" chemical system.†

ORGANIC SYNTHESSES IN LIQUID SULFUR DIOXIDE

The non-flammability, low reactivity, high solvent power towards covalent compounds and the relative convenience of use at low temperatures possessed by liquid sulfur dioxide have made it an important medium for carrying out certain organic syntheses. The solvent is of particular utility in syntheses where side reactions may occur at higher temperatures.

The Friedel-Crafts reaction proceeds smoothly and with high yield in liquid sulfur dioxide (43), the formation of sulfinic acids as products of secondary reaction being almost entirely eliminated. The relatively high solubility of aluminum chloride, approximately 8 grams per 100 grams of liquid sulfur dioxide at $-8^{\circ}\text{C}.$, certainly enhances the efficiency of this process. In the preparation of phenol esters, the possibility of a Fries rearrangement is reduced at the low temperatures (-8° to $-10^{\circ}\text{C}.$) at which reaction is carried out. The results of a study of the Friedel-Crafts reaction in liquid sulfur dioxide medium are presented in Table 69.

* Pertinent references on this subject are: Bright and Jasper, *J. Am. Chem. Soc.*, **63**, 3486 (1941); **65**, 1262 (1943); **66**, 105 (1944). Burg, *J. Am. Chem. Soc.*, **65**, 1629 (1943). Moede and Curran, *J. Am. Chem. Soc.*, **71**, 852 (1949).

† Recent work strongly suggests that the proposed mode for the auto-ionization of liquid sulfur dioxide, which has been utilized by Jander, is of minor importance with regard to the ionic species present in this solvent. Radioactive sulfur (S^{35}) has been found to exchange rapidly between liquid sulfur dioxide and the "base-analogous" pyrosulfite ion. On the other hand, exchange between sulfur dioxide and the "acid-analogous" thionyl compounds (SOBr_2 and SOCl_2) is extremely slow [Johnson, Norris, and Huston, *J. Am. Chem. Soc.*, **73**, 3052 (1951)]. This slow exchange indicates that thionyl compounds (and also liquid sulfur dioxide) yield a negligible amount of SO^{++} ion, and would thus appear to necessitate a modification of Jander's conception of simple ionic mechanisms for reactions involving thionyl compounds (for example, neutralization reactions). On the basis of the exchange studies cited above and others [Nakata, *J. Chem. Soc. Japan*, **64**, 635 (1943); Huston, *J. Am. Chem. Soc.*, **73**, 3049 (1951)], it has been suggested that acid-base phenomena in liquid sulfur dioxide can be interpreted better in terms of the mobility of oxide ions, analogous to the mobility of hydrogen ions in water.

TABLE 69

A STUDY OF THE FRIEDEL-CRAFTS REACTION IN LIQUID SULFUR DIOXIDE

(AlCl₃, catalyst; volume SO₂, 300 cc.; temperature, -8° to -10°C.)

<i>Reactants</i>	<i>Molar Ratios, Ar:RCl:AlCl₃</i>	<i>Yields of Products</i>
Benzene and <i>tert</i> -amyl chloride	0.3:0.25:0.06	46% mixed amylbenzenes
Naphthalene and benzoyl chloride	0.25:0.25:0.3	52% α -benzoylnaphthalene
Benzene and benzoyl chloride	0.2:0.1:0.11	84% benzophenone
Phenol and <i>tert</i> -amyl chloride	0.25:0.25:0.3	50% <i>tert</i> -amylphenol
Veratrole and acetyl chloride	0.1:0.1:0.08	82% acetoveratrole
Phenol and benzoyl chloride	0.25:0.25:0.3	94% phenylbenzoate
Phenol and benzoyl chloride	0.12:0.25:0.3	70% phenylbenzoate and 30% <i>p</i> -benzoylphenyl- benzoate
Resorcinol and benzoyl chloride	0.12:0.25:0.3	75% resorcinol dibenzoate

Liquid sulfur dioxide has been used as a solvent for the preparation of carbyl sulfates by interaction of sulfonating agents and aliphatic or hydroaromatic alcohols or the corresponding olefins (44, 45). For instance, lauryl alcohol undergoes quantitative conversion to the sulfate when treated with chlorosulfonic acid.

Sulfur dioxide is an excellent medium for the sulfonation of aromatic compounds (45, 46, 47). The reaction between aromatic hydrocarbons and chlorosulfonic acid or sulfur trioxide is readily controlled, reasonably rapid, and results in very high yields of the sulfonated product. Moreover, the products are not contaminated with inorganic salts and are thus readily purified.

Brominations have also been carried out in this solvent (43). Bromine is readily soluble, and the resulting solution can be used as a medium for the addition of the halogen to unsaturated compounds, as well as for direct substitution. In the absence of catalysts, there is little sulfone formation. Thus styrene is converted quantitatively to styrene dibromide; *p*-bromophenol is obtained from phenol in over 90% yield.

A noteworthy and potentially valuable side light to the use of solutions of bromine in liquid sulfur dioxide is the fact that such solutions, by treatment with water, can readily be converted to media containing anhydrous hydrogen bromide (43). The stoichiometry of this conversion is shown below:



Reaction between styrene and a solution of hydrogen bromide so prepared results in the formation of α -bromophenylethane in over 70% yield.

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ACID CHLORIDES

The highly successful application of the solvent system theory of acids, bases, and salts to liquid sulfur dioxide has already been described. The extension of this idea to include the acid chlorides, a group of solvents which, like sulfur dioxide are non-protonic, has, with two notable exceptions, proved less fruitful, primarily because of the inherent reactivity of these substances. Of the various acid chlorides studied, only for selenium(IV) oxychloride and carbonyl chloride is there considerable experimental evidence available which demonstrates that these substances may be regarded as parent solvents. In addition to the relatively large amount of work which has been done with selenium(IV) oxychloride and carbonyl chloride, there are fragmentary reports on the utilization of nitrosyl chloride, phosphorus(V) and vanadium(V) oxychlorides, and thionyl and sulfuryl chlorides * as media for chemical reactions. At least two of these, namely nitrosyl chloride and phosphorus(V) oxychloride, appear to be worthy of more intensive investigation.

SELENIUM(IV) OXYCHLORIDE, SeOCl_2

PREPARATION AND PHYSICAL PROPERTIES. Selenium(IV) oxychloride was first prepared by Weber (1) in 1859 by heating together the vapors of selenium dioxide and selenium tetrachloride:



Extensive work by Lenher (2, 3) has demonstrated that selenium(IV) oxychloride may be made conveniently by the dehydration of

* Thionyl and sulfuryl chlorides appear to be fair ionizing media, but their usefulness is limited by their high chemical reactivity and inability to dissolve salts to any appreciable extent [Walden, *Z. anorg. Chem.*, **25**, 209 (1900); Silberrad, *Chem. and Ind.*, **45**, 36, 55 (1926)]. The insolubility of nearly all salts tested in vanadium(V) oxychloride definitely eliminates this substance as a useful medium for inorganic reactions [Brown and Synder, *J. Am. Chem. Soc.*, **47**, 2671 (1925); Brown and Griffiths, *Iowa State Coll. J. Sci.*, **9**, 89 (1934)].

$\text{SeO}_2 \cdot 2\text{HCl}$ with concentrated sulfuric acid. The product may be purified readily by distillation under reduced pressure.

Pure selenium(IV) oxychloride is obtained as a straw-colored liquid. Its important physical properties are summarized in Table 70.

TABLE 70

SOME PHYSICAL CONSTANTS OF SELENIUM(IV) OXYCHLORIDE

<i>Property</i>	<i>Value</i>	<i>Reference</i>
Freezing point, °C.	10.9	(3)
Boiling point, °C.	176	(3)
Specific conductivity, ohm^{-1}	$2.0(\pm 0.3) \times 10^{-5}$ (25°C.)	(4)
Density, g./cc.	2.424 (22°C.)	(3)
Dielectric constant	46.2 ± 1 (20°C.)	(5)

The freezing and boiling point values would appear to indicate that the solvent is useful as a liquid medium for chemical reactions over a wide temperature range. Unfortunately this is not the case. Frequently, its behavior at elevated temperatures, and, occasionally at lower temperatures, is not that of an inert medium, but rather that of a powerful oxidizing agent. In view of its high specific conductance, which is of the same order of magnitude as that of liquid hydrogen fluoride, it is not surprising that selenium(IV) oxychloride is also a powerful solvolyzing agent.

SOLVENT PROPERTIES. The solubility studies of Lenher (6, 7) and Ray (8) serve to emphasize the great reactivity of selenium(IV) oxychloride toward many substances. Among the non-metals, sulfur, selenium, tellurium, bromine, and iodine are readily soluble in the cold; at elevated temperatures the first three react with the solvent, with the formation of sulfur monochloride, selenium monochloride, and tellurium(IV) chloride, respectively. Red phosphorus reacts in the cold with the evolution of light and heat, whereas the white form undergoes explosive reaction. Boron, silicon, and carbon are insoluble and unreactive (6).

Most metals react with selenium(IV) oxychloride to form the corresponding chlorides, selenium monochloride, and selenium dioxide. It is reported that potassium explodes in the cold in the presence of the solvent but that sodium is unattacked (6). Copper, silver, lead, nickel, cobalt, iron, antimony, bismuth, and tin react with varying degrees of readiness (6, 8).

Many metal oxides, carbonates, and sulfides undergo solvolysis, with the formation of the metal chlorides (6, 7, 8). Strong oxidizing

agents, such as iodic and periodic acids, potassium bromate and persulfate, react with selenium(IV) oxychloride to liberate chlorine.

The only comprehensive quantitative study dealing with the solubility of inorganic compounds in selenium(IV) oxychloride has been that of Wise (9) on metal chlorides. The data obtained by Wise are shown in Table 71. Solvate formation generally accompanies high solubility.

TABLE 71

THE SOLUBILITIES OF METAL CHLORIDES IN SELENIUM(IV) OXYCHLORIDE

<i>Metal</i>	<i>Solubility, grams/100 g. of Solution</i>	<i>Solvates Formed</i>
Li	3.21	
Na	0.57	
K	2.89	$\text{KCl} \cdot \text{SeOCl}_2$
Rb	3.56	$\text{RbCl} \cdot \text{SeOCl}_2$
Cs	3.83	Of indefinite character
Mg	4.96	$\text{MgCl}_2 \cdot 3\text{SeOCl}_2$
Ca	6.11	$\text{CaCl}_2 \cdot 3\text{SeOCl}_2$
Sr	5.17	
Ba	3.95	
Zn	1.10	
Cd	0.15	
Hg	0.89	
Cu(II)	insol.	
Ag	insol.	
Ti(IV)	0.75	$\text{TiCl}_4 \cdot 2\text{SeOCl}_2$
Sn(IV)	13.73	$\text{SnCl}_4 \cdot 2\text{SeOCl}_2$
Pb(II)	insol.	
As(III)	miscible in all proportions	
Sb(V)	38.64	$\text{SbCl}_5 \cdot 2\text{SeOCl}_2$
Cr(III)	insol.	
Mn(II)	0.16	
Fe(III)	23.40	$\text{FeCl}_3 \cdot 2\text{SeOCl}_2$
Ni(II)	0.15	
Co(II)	0.17	

Qualitatively, the solubility of most of the chlorides increases with increasing temperature, the solubility of barium chloride being a notable exception. It should be noted that the solubility of most of the covalent metal halides which have been studied is usually high.

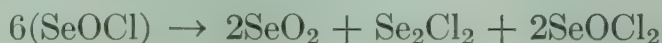
There are few cases in which organic compounds dissolve in selenium(IV) oxychloride without reaction. Saturated hydrocarbons are immiscible with the solvent, whereas carbon tetrachloride, chloroform, carbon disulfide, and benzene are miscible in all proportions (6). However, even carbon tetrachloride is slowly attacked, the products of reaction being selenium tetrachloride and carbonyl chloride.

ACID-BASE RELATIONSHIPS IN SELENIUM(IV) OXYCHLORIDE. Available information concerning the role that selenium(IV) oxychloride plays as a parent solvent is derived from the brilliant work of G. B. L. Smith and his collaborators (10, 11, 12) on acid-base relationships in this medium. According to Smith (10), selenium(IV) oxychloride may be considered to undergo the following auto-ionization:



Credence is lent to such a postulation by a number of pertinent experimental observations.

1. The large value for the specific conductance indicates that the ion concentrations in the pure liquid are relatively great. Upon electrolysis of the pure substance, chlorine is liberated at the anode, and selenium monochloride is probably formed at the cathode. The electrolysis of potassium chloride or tin(IV) chloride in selenium(IV) oxychloride yields chlorine as the anode product and selenium dioxide and selenium monochloride as cathode products. It appears reasonable, therefore, to formulate the following equations for the electrolytic decomposition of the solvent:



2. The nature of the products of the solvent action of selenium(IV) oxychloride on various metals (6, 8) is such that an explanation of the reaction in terms of the auto-ionization postulated by Smith is entirely reasonable. For example, the analytical data obtained for the reaction between copper and the solvent suggest the following mechanism:



3. The suggested auto-ionization has also proved exceedingly useful in correlating the behavior of a large number of substances in terms of acid and base phenomena in the solvent. Smith (10), influenced by the original proposals of Lewis (13), defines an acid in any solvent as a solute which is an electron-pair acceptor toward that solvent, and a base as a solute which is an electron-pair donor toward the solvent. Thus chlorides of non-metals or of amphoteric elements may be re-

garded as acids in selenium(IV) oxychloride, and such substances as ammonia, pyridine, and quinoline may be considered to function as bases.* Typical reactions for an acid and base, respectively, with the solvent are given below:



It should be pointed out that the Cady and Elsey (14) definitions of acids and bases are equally applicable here. Examination of the equations given above shows that an acid increases the concentration of the SeOCl^+ ion, the cation postulated to be characteristic of the solvent, whereas a base gives rise to the characteristic chloride ion.

The disolvates of titanium(IV), tin(IV), and iron(III) chlorides (see Table 72) may be formulated in terms which are consistent with the auto-ionization of the parent solvent and with the acid and base definitions which have been proposed.

TABLE 72

DISOLVATES OF CERTAIN CHLORIDES

<i>Solvate</i>	<i>Formulation</i>
$\text{TiCl}_4 \cdot 2\text{SeOCl}_2$	$2\text{SeOCl}^+, \text{TiCl}_6^-$
$\text{SnCl}_4 \cdot 2\text{SeOCl}_2$	$2\text{SeOCl}^+, \text{SnCl}_6^-$
$\text{FeCl}_3 \cdot 2\text{SeOCl}_2$	$2\text{SeOCl}^+, \text{FeCl}_5^-$

These formulations are in concordance with the observation that such metals as magnesium, calcium, lead, mercury, copper, zinc, and sodium are in general more reactive and more soluble in a 20% solution of tin(IV) chloride than in selenium(IV) oxychloride alone (10).†

A formulation analogous to that offered above is also applicable as an explanation for the powerful solvent action of solutions of sulfur trioxide in selenium(IV) oxychloride. Such solutions are capable of dissolving oxides of aluminum, chromium, the rare earths, titanium, niobium, molybdenum, vanadium, and uranium (6). According to

* Chlorides of the alkali and alkaline earth metals may be regarded as incidental bases in selenium(IV) oxychloride, inasmuch as they furnish the chloride ion, the anion postulated to be characteristic of the solvent (10, 12). It is probable that in the monosolvates of potassium and rubidium chlorides isolated by Wise (9) (see Table 71) it is the chloride ion, rather than the alkali metal ion, which is solvated (11).

† Analogous observations by Germann (15) on the reactivity of a solution of aluminum chloride in phosgene toward metals, as compared with the reactivity of phosgene alone, will be described later.

Smith (10), the active agent in such solutions is a chlorosulfonic acid of the selenium(IV) oxychloride system, $(\text{SeOCl})(\text{SO}_3\text{Cl})$, formed as a result of the ability of sulfur trioxide to act as an electron pair acceptor toward chloride ions furnished by the solvent.

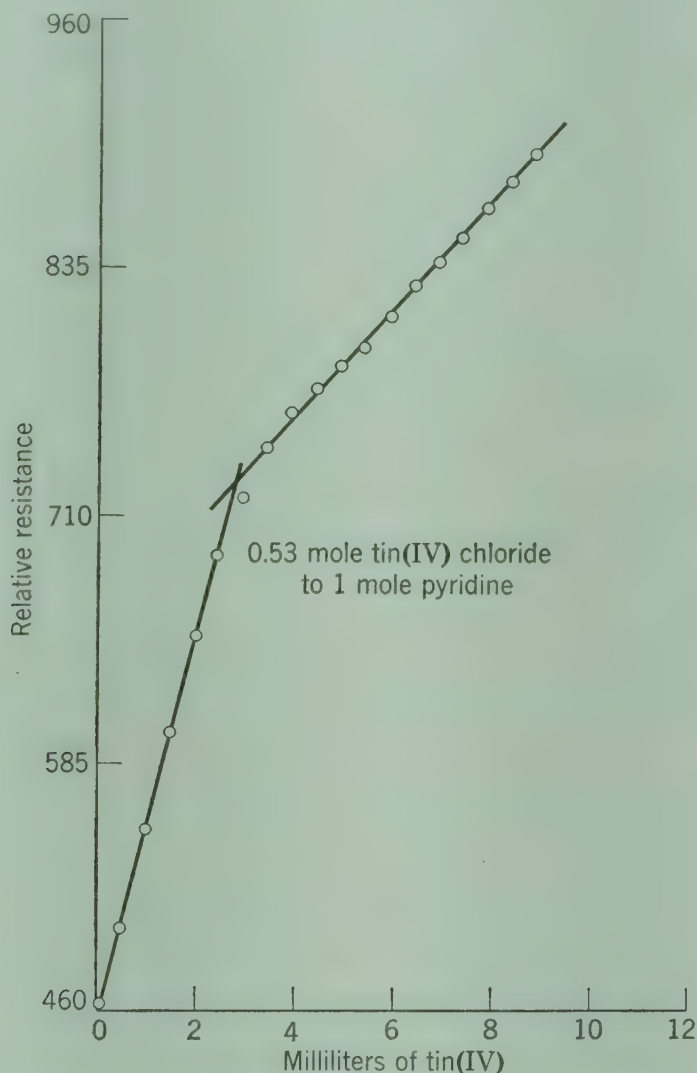


FIGURE 28. Conductometric titration of a solution of pyridine in selenium(IV) oxychloride with a solution of tin(IV) chloride in selenium(IV) oxychloride.

It has already been indicated that such compounds as ammonia, pyridine, and quinoline, in their function as bases, act as electron donors toward selenium(IV) oxychloride. Ammonia reacts with selenium(IV) oxychloride to give at least two solvates, one probably the monosolvate and the other a higher solvate of undetermined composition (10). Pyridine, quinoline, and isoquinoline form well-defined mono- and disolvates (11). These compounds possess a relatively high degree of stability. The disolvates are not decomposed at 61°C . in the case of quinoline and isoquinoline, whereas the pyridine com-

TABLE 73

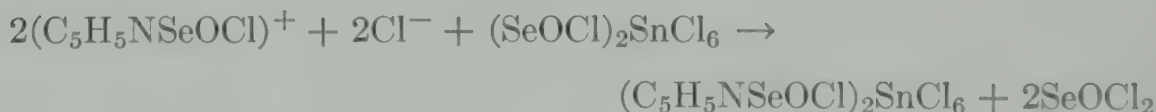
CONDUCTOMETRIC ACID-BASE TITRATIONS IN SELENIUM(IV) OXYCHLORIDE

<i>System</i>	<i>Titrant</i>	<i>Stoichiometric Ratios Indicated</i>
SnCl ₄ -C ₅ H ₅ N	SnCl ₄	1SnCl ₄ , 2C ₅ H ₅ N
SnCl ₄ -C ₅ H ₅ N	C ₅ H ₅ N	2SnCl ₄ , 1C ₅ H ₅ N
		1SnCl ₄ , 1C ₅ H ₅ N
		1SnCl ₄ , 2C ₅ H ₅ N
		1SnCl ₄ , 3C ₅ H ₅ N
SnCl ₄ -KCl	SnCl ₄	2SnCl ₄ , 3KCl *
		1SnCl ₄ , 1KCl
SnCl ₄ -CaCl ₂	CaCl ₂	2SnCl ₄ , 1CaCl ₂
		1SnCl ₄ , 1CaCl ₂
		2SnCl ₄ , 3CaCl ₂
FeCl ₃ -C ₅ H ₅ N	C ₅ H ₅ N	1FeCl ₃ , 1C ₅ H ₅ N
		1FeCl ₃ , 2C ₅ H ₅ N
		1FeCl ₃ , 3C ₅ H ₅ N
SO ₃ -C ₅ H ₅ N	C ₅ H ₅ N	1SO ₃ , 1C ₅ H ₅ N
		1SO ₃ , 2C ₅ H ₅ N
AsCl ₃ -C ₅ H ₅ N	C ₅ H ₅ N	2AsCl ₃ , 1C ₅ H ₅ N
		1AsCl ₃ , 1C ₅ H ₅ N
		1AsCl ₃ , 2C ₅ H ₅ N

* This value is erroneously recorded in a table in the original article (see reference 10, p. 174), probably owing to a typographical error.

pound is slowly converted to the monosolvate at this temperature. In harmony with the acid and base definitions, it is proposed that the monosolvate be considered to consist of RSeOCl⁺ and Cl⁻ ions.*

On the basis of the proposed acid and base definitions, neutralization reactions may be characterized by reactions between electron pair donors toward the solvent with electron pair acceptors. Such reactions have been studied in selenium(IV) oxychloride both by conductometric and potentiometric methods by Smith and his collaborators (10, 12). For example, the titration of a solution of pyridine in selenium(IV) oxychloride with tin(IV) chloride solution (Figure 28) shows the formation of a compound containing two moles of the former substance for each mole of the latter. The following equation describes the reaction:



* The fact that a solution of pyridine in selenium(IV) oxychloride is an excellent conductor of the electric current (10) indicates that ionic species play an important role in the constitution of the solvates.

A summary of the titrations which have been carried out and the stoichiometric ratios of the reactants in the compounds formed is given in Table 73.

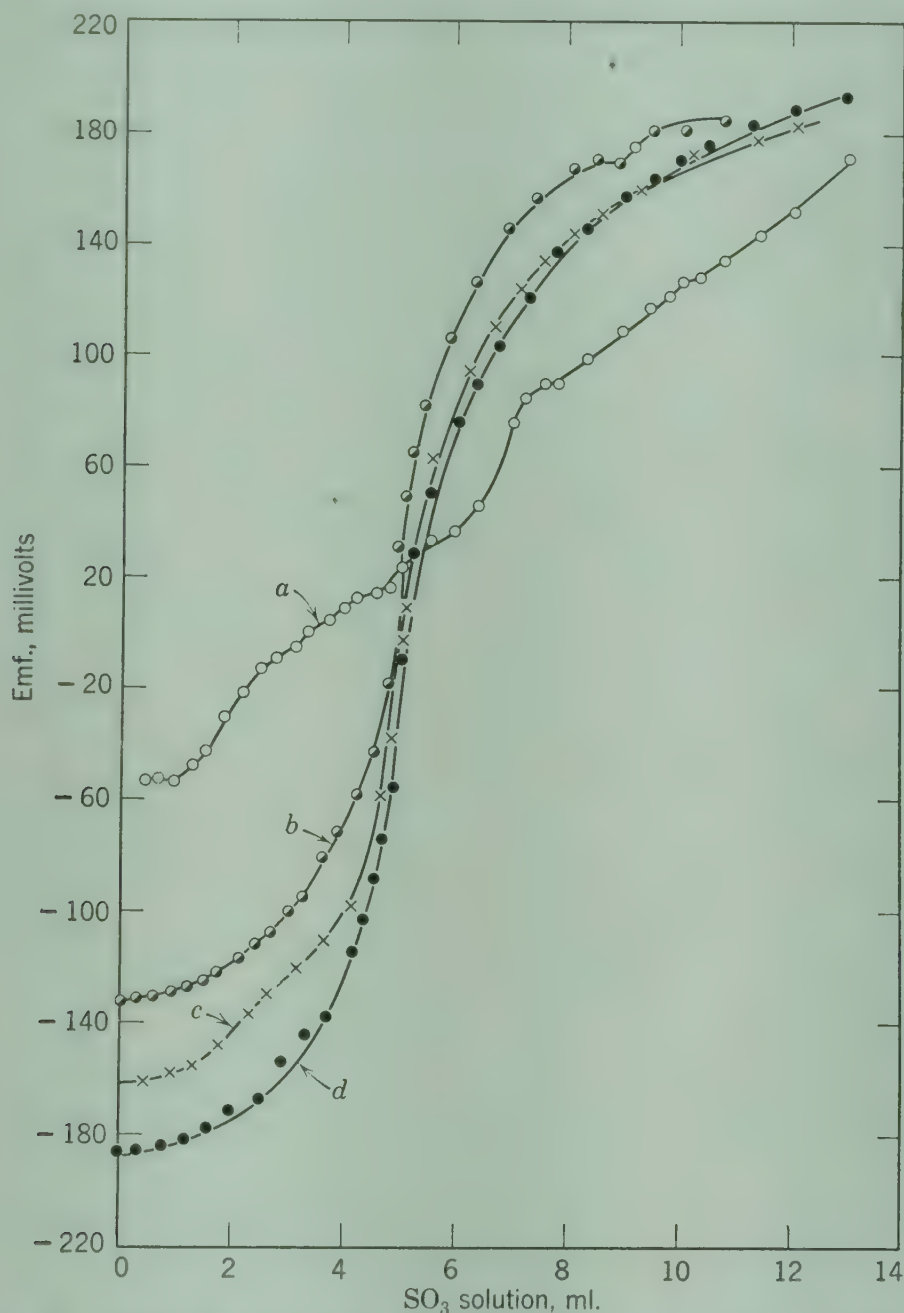


FIGURE 29. Titration curves in selenium(IV) oxychloride. (a) Potassium chloride, (b) pyridine, (c) quinoline, and (d) isoquinoline with sulfur trioxide.

Modifications of a potentiometric technique employing concentration cells have been adapted for the study of neutralization reactions in selenium(IV) oxychloride (12). Titration curves, similar to those found for neutralization reactions in water, are obtained for reactions between non-protonic acids and non-protonic bases. Figures 29 and 30 show, respectively, the titration curves for the bases potassium

chloride, pyridine, quinoline, and isoquinoline with the acid sulfur trioxide; and for the acids sulfur trioxide, iron(III) chloride, and tin(IV) chloride with the base quinoline. The titration curves indicate that

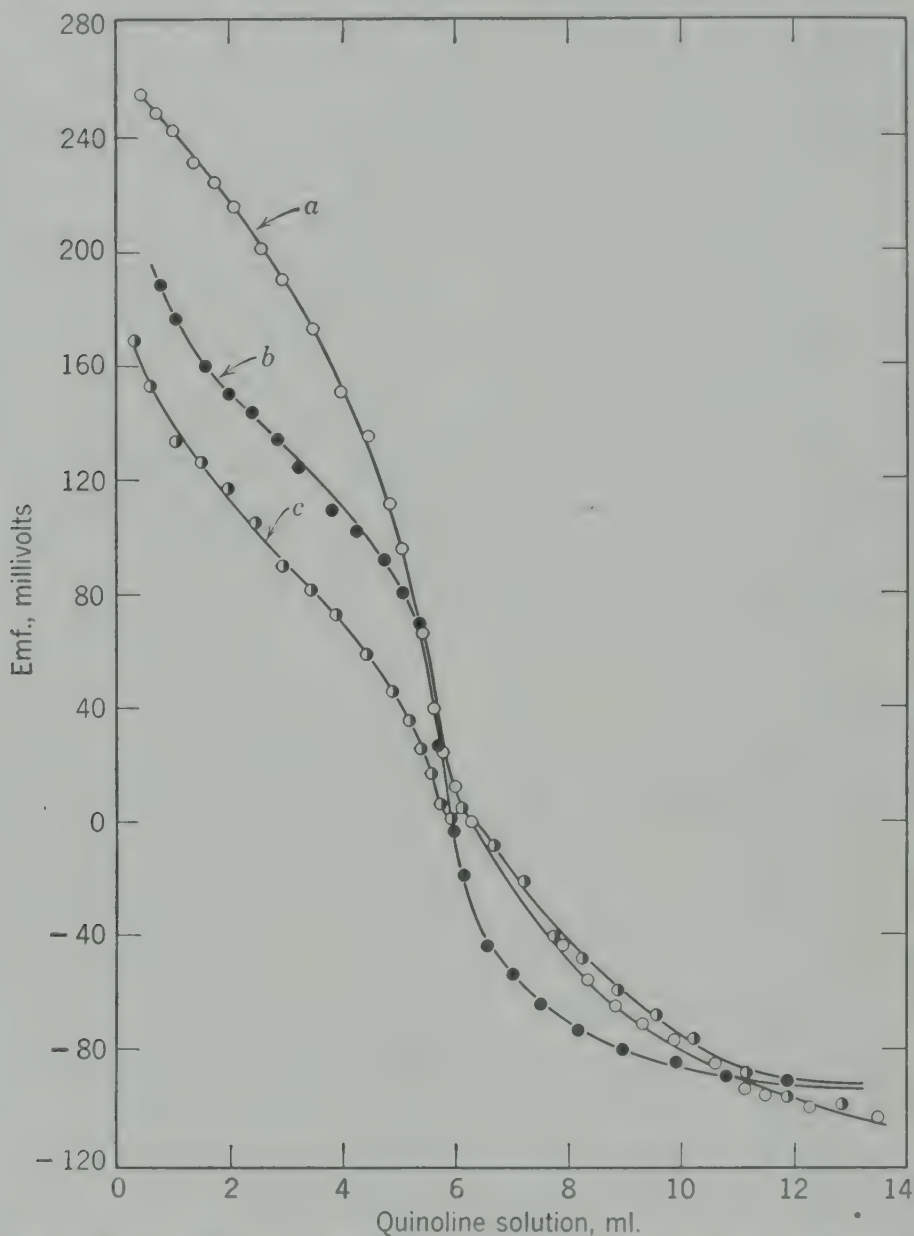


FIGURE 30. Titration curves in selenium(IV) oxychloride. (a) Sulfur trioxide, (b) iron(III) chloride, and (c) tin(IV) chloride with quinoline.

the neutralization reactions are of the weak acid-weak base type. The orders of relative base and acid strengths as determined by the titrations are the following:

Relative base strengths:

isoquinoline > quinoline > pyridine > potassium chloride

Relative acid strengths:

sulfur trioxide > iron(III) chloride > tin(IV) chloride

CARBONYL CHLORIDE (PHOSGENE), COCl_2

PREPARATION AND GENERAL PROPERTIES. Carbonyl chloride (phosgene) was first obtained by John Davy in 1811 by the exposure of equal quantities of carbon monoxide and chlorine to sunlight (16). This reaction still serves as one of the principal methods for the preparation of the compound. Other useful methods for obtaining carbonyl chloride are: (a) the oxidation of chlorinated hydrocarbons by means of chromic acid; (b) the interaction of sulfur trioxide or fuming sulfuric acid with chlorinated hydrocarbons; and (c) the direct combination of carbon monoxide and chlorine in the presence of such catalysts as spongy platinum, animal charcoal, or activated wood charcoal (17). For uses involving precision measurements carbonyl chloride may be purified by an elaborate process of fractional distillation (18).

The values of some important physical constants of carbonyl chloride which are shown in Table 74 serve to emphasize some of the limitations encountered in the use of the material as a medium for chemical reactions.

TABLE 74

SOME PHYSICAL CONSTANTS OF CARBONYL CHLORIDE

<i>Property</i>	<i>Value</i>	<i>Reference</i>
Freezing point, °C.	-128	(19)
Boiling point, °C.	8.2 (756 mm.)	(20)
Specific conductivity, ohm^{-1}	7×10^{-9} (25°C.)	(21)
Density, g./cc.	1.435 (0°C.)	(19)
Dielectric constant	4.34 ± 0.02 (22°C.)	(22)

It is apparent that the unfavorable liquid range of carbonyl chloride makes it a rather difficult solvent with which to work. Its utility is further limited by its intolerable odor, extremely poisonous character, sensitivity to moisture, and generally high chemical reactivity. Moreover, as would be expected from the low value of the dielectric constant, carbonyl chloride is a very poor solvent for most inorganic substances. Nevertheless, sufficient experimental data have been accumulated concerning inorganic reactions in carbonyl chloride to permit an extension of the solvent system theory to this medium.

SOLVENT PROPERTIES AND ACID-BASE RELATIONSHIPS. Carbonyl chloride is capable of dissolving few inorganic substances (20). These are covalent in character and include elementary iodine, iodine(III) chloride, arsenic(III) and antimony(III) chlorides, antimony(V) chloride, the various sulfur chlorides (20) and aluminum chloride (23).

It was first demonstrated by Germann (24) that solutions of aluminum chloride in carbonyl chloride possess high chemical reactivity. An intensive study of the behavior of solutions of aluminum chloride in carbonyl chloride by Germann and his collaborators contributed significantly to the development of the present concept regarding acid-base relationships in this medium (15, 18, 21, 24, 25, 26, 27, 28) and related non-protonic solvents. The isolation of the compound $\text{Al}_2\text{Cl}_6 \cdot 5\text{COCl}_2$ from carbonyl chloride solutions of aluminum chloride leaves no doubt but that the latter exists in a solvated condition in this medium (23). The specific conductivity of such solutions increases with increasing concentration of aluminum chloride, and the more concentrated solutions conduct nearly one hundred thousand times as well as pure liquid carbonyl chloride (21, 28). The tremendous increase in conductivity is indicative of ion formation through interaction of solute and solvent. Electrolysis of such solutions results in the liberation of carbon monoxide and chlorine.

Whereas liquid carbonyl chloride is inert toward such metals as potassium, magnesium, calcium, zinc, and cadmium, its solutions with aluminum chloride attack these metals readily, with the evolution of carbon monoxide (18, 25). The quantitative extent of reaction is proportional to the amount of aluminum chloride present, provided both metal and carbonyl chloride are present in excess. The reaction with calcium has been studied in some detail and yields a crystalline product of the composition $\text{CaCl}_2 \cdot 2\text{AlCl}_3 \cdot 2\text{COCl}_2$. This substance has a decomposition pressure of about 25 mm. of mercury at 19.5° and is readily "dephosgenated" to give $\text{CaCl}_2 \cdot 2\text{AlCl}_3$. [This compound may be formulated as $\text{Ca}(\text{AlCl}_4)_2$.]

Ionic chlorides, like other electrovalent compounds, are insoluble in liquid carbonyl chloride; their solubility may be markedly increased, however, by the addition of aluminum chloride. From the resulting solutions complexes may be isolated which are analogous to those formed by the action of calcium as described in the preceding paragraph (26, 27). For example, the dissolution of calcium chloride in a carbonyl chloride solution of aluminum chloride, followed by the removal of some of the solvent, results in the crystallization of the solvate $\text{CaCl}_2 \cdot 2\text{AlCl}_3 \cdot 2\text{COCl}_2$ which has been described above. In contrast to the insolubility of calcium chloride, this solvate is soluble to the extent of 100 g. per 100 g. of solvent (26). Some "dephosgenated" complexes have been prepared by sealed tube reactions at 100°C . between metal chloride and aluminum chloride in carbonyl chloride medium (27). Vapor pressure curves of the complex-carbonyl chloride systems at 25°C . show the formation of a number of solvates.

The compositions of the solvates, which have been identified, and their vapor pressures are given in Table 75. Carbonyl chloride solutions of

TABLE 75

SOLVATES IDENTIFIED IN $M_x(\text{AlCl}_4)_y\text{-COCl}_2$ SYSTEMS

<i>Complex</i>	<i>Composition of Solvate</i>	<i>Vapor Pressure, mm. of Hg, 25°C.</i>
$\text{Na}(\text{AlCl}_4)$	No solvate formed	...
$\text{Sr}(\text{AlCl}_4)_2$	$\text{Sr}(\text{AlCl}_4)_2 \cdot \text{COCl}_2$	175
	$5\text{Sr}(\text{AlCl}_4)_2 \cdot 9\text{COCl}_2$	950
$\text{Ba}(\text{AlCl}_4)_2$	$\text{Ba}(\text{AlCl}_4)_2 \cdot \text{COCl}_2$	290
	$3\text{Ba}(\text{AlCl}_4)_2 \cdot 8\text{COCl}_2$	625

these complexes are much better conductors of the electric current than the solution of aluminum chloride itself (15, 29). Electrolysis of a solution of $\text{Ca}(\text{AlCl}_4)_2$ results in the primary deposition of calcium at the cathode and the evolution of chlorine at the anode.

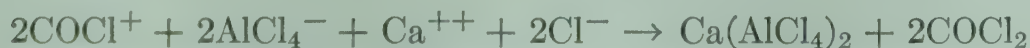
The various phenomena which have been discussed in this section may be best interpreted in the following manner. According to Germann (15, 26, 28),* aluminum chloride may be considered to possess the characteristics of a typical acid in carbonyl chloride solution. Reaction with carbonyl chloride may be assumed to increase the concentration of cations characteristic of the solvent in the following fashion (30):



The resulting acid solution is capable of reacting with metals in a manner entirely analogous to that of metal-acid reactions in water:



Reaction of an aluminum chloride solution with an ionic metal chloride is a typical neutralization reaction, since any substance yielding chloride ion in solution may be regarded as a base:



* This discussion embodies the essential concepts of Germann, but formulation of these concepts is in terms more consistent with current ideas of auto-ionization of non-protonic solvents and the nature of anionic aluminum complexes.

OTHER ACID CHLORIDES

NITROSYL CHLORIDE, NOCl. A report by Burg and Campbell (31) on liquid nitrosyl chloride as an ionizing medium indicates some potentialities for this substance as a parent solvent for an acid-base system. On the basis of its dielectric constant, 18.2 at 12°C. (32), liquid nitrosyl chloride would be expected to be a fairly effective ionizing solvent. The value for the specific conductivity, $2.88 \times 10^{-6} \text{ ohm}^{-1}$ at -20°C ., indicates a relatively high degree of self-ionization, which probably occurs in the following manner:



Substances giving rise to the nitrosyl ion may be expected to act as acids in this medium, and those yielding chloride ion would behave as bases. Potassium chloride is insoluble in liquid nitrosyl chloride and contributes no conductance effect. The nitrosyl ion is apparently strongly solvated in nitrosyl chloride. Nitrosyl salts are soluble and good conductors of the electric current as is borne out by the data in Table 76. Further evidence that the highly soluble nitrosyl salts are

TABLE 76

CONDUCTANCES OF NITROSYL SALTS IN LIQUID NITROSYL CHLORIDE

<i>Solute</i>	<i>Molarity</i>	<i>Temp., °C.</i>	<i>Specific Conductance, ohm⁻¹</i>	<i>Molar Conductance</i>
NO(AlCl ₃)	0.098	-20	1.17×10^{-2}	119
NO(FeCl ₃)	0.0099	-20	1.34×10^{-3}	136
NO(FeCl ₃)	0.0094	-44	1.00×10^{-3}	106
NO(SbCl ₅)	0.140	-20	2.35×10^{-2}	168
NO(SbCl ₅)	0.140	-44	2.20×10^{-2}	157
NOCl	Pure	-20	2.88×10^{-6}	...

solvated in solution is indicated by the isolation of NOAlCl₃·NOCl as a reaction product between gaseous nitrosyl chloride and NO(AlCl₃). The solvate exhibits a dissociation pressure of about 240 mm. of mercury at 0°C.

An attempt to dissolve potassium chloride in a solution of NO(SbCl₅) in nitrosyl chloride proved unsuccessful, possibly because of the formation of a protective coating of K(SbCl₅). Had this reaction succeeded, it would have been analogous to the solvent action of carbonyl chloride solutions of aluminum chloride on metal chlorides.*

* It has been demonstrated that [(CH₃)₄N]Cl is a soluble base in the nitrosyl chloride system. A conductometric titration of FeCl₃·NOCl with this base reveals

PHOSPHORUS (V) OXYCHLORIDE, POCl_3 . The use of phosphorus(V) oxychloride as a solvent for chemical reactions is worthy of really serious investigation. A readily available and relatively cheap material, it is in general a better solvent for inorganic substances than liquid sulfur dioxide. The value of the specific conductance, 1.71×10^{-6} at 25°C . (33), indicates that phosphorus(V) oxychloride undergoes a degree of auto-ionization comparable to that of water. Its dielectric constant [13.9 at 22°C . (34)] is of the same order of magnitude as that of liquid sulfur dioxide. The few available data on the conductances of salts in phosphorus(V) oxychloride indicate that it is a good ionizing solvent for binary compounds (35). The material possesses a convenient liquid range [freezing point, 1.25°C . (36); boiling point, 105.8°C . at 753 mm. (35)] for experimental work. One of the chief objections to the use of phosphorus(V) oxychloride as a medium for chemical reactions is its relatively great reactivity, particularly toward water.

Methods for the preparation of phosphorus(V) oxychloride involve either (a) reaction between phosphorus(V) oxide and phosphorus(V) chloride or (b) the chlorination of phosphate rock (37, 38). For use in exact experimental work the compound may be separated from phosphoric acid and hydrogen chloride impurities by distillation, and then further purified by redistillation from potassium in an inert atmosphere (39). A more convenient method of purification involves the repeated distillation of the material after it has been permitted to stand over freshly activated silica gel (40).

No systematic investigation of solubilities in phosphorus(V) oxychloride has been carried out. The qualitative solubilities of some inorganic substances as obtained from several studies are summarized in Table 77 (35, 39, 41). Most of the inorganic salts which dissolve in phosphorus(V) oxychloride give colored solutions.

A large number of non-polar halides form readily isolable solvates with phosphorus(V) oxychloride. Colorless crystals of $\text{BCl}_3 \cdot \text{POCl}_3$

the occurrence of what may be regarded as a typical neutralization reaction, which may be formulated in the following manner:



The plot obtained for the conductometric titration is that expected for the addition of a moderately strong base to a strong acid.

That the addition compound $\text{FeCl}_3 \cdot \text{NOCl}$ may be formulated as $\text{NO}(\text{FeCl}_4)$ is supported by electrolysis of this compound in nitrosyl chloride. Nitric oxide and chlorine are liberated at the cathode and anode, respectively, and iron migrates slowly toward the anode. (McKenzie, Ph.D. Thesis, University of Southern California, 1950.)

TABLE 77

QUALITATIVE SOLUBILITIES OF INORGANIC SUBSTANCES IN PHOSPHORUS(V)
OXYCHLORIDE

<i>Appreciably Soluble</i>			<i>Slightly Soluble</i>	<i>Insoluble</i>	
NaI (solvolized)	AsBr ₃	PCl ₃	KClO ₄	LiCl	CuCl ₂
KI (solvolized)	AsI ₃	PCl ₅	KIO ₄	NaCl	ZnCl ₂
RbI (solvolized)	SbBr ₃	PBr ₃	KMnO ₄	KCl	Hg ₂ Cl ₂
KClO ₃	SbI ₃	PBr ₅	CdI ₂	LiBr	MnCl ₂
KBrO ₃	SbCl ₅	SO ₃	Hg(CN) ₂	NaBr	CrO ₃
KIO ₃	FeCl ₂	Cl ₂ O ₇		KBr	P ₄ O ₁₀
K ₂ CrO ₄	FeCl ₃	Br ₂		KNO ₃	I ₂ O ₅
K ₂ Cr ₂ O ₇	CoI ₂	I ₂		K ₃ [Fe(CN) ₆]	
CuBr	PtCl ₄	ICl		K ₂ C ₂ O ₄	
AuCl ₃	CCl ₄	ICl ₃		CaCl ₂	
HgI ₂	SiCl ₄	[(CH ₃) ₄ N]I		SrCl ₂	
SnI ₄	SiBr ₄	[(C ₂ H ₅) ₄ N]I		BaCl ₂	
AsF ₃	N ₂ O ₅	[(CH ₃) ₃ S]I		CdBr ₂	
AsCl ₃					

melting at 73°C. have been obtained from the interaction of the two components (42). BBr₃·POCl₃ has also been reported (41). Reaction between aluminum chloride and phosphorus(V) oxychloride yields the insoluble solvate Al₂Cl₆·2POCl₃ melting at 165°C. (43). This reaction is of some practical importance in that it affords a method for complete removal of aluminum chloride from Friedel-Crafts mixtures (44).

No solvates have been described for carbon and silicon tetrachlorides and silicon tetrabromide, compounds which are appreciably soluble in phosphorus(V) oxychloride. However, the compound 2SnCl₄·POCl₃, which is soluble in an excess of the solvent, has been isolated (41), and SnCl₄·2POCl₃ has also been described (45). The action of the oxychloride on titanium(IV) fluoride and tellurium(IV) oxide results in the formation of TiCl₄·2POCl₃ and TeCl₄·POCl₃, respectively (46, 47); the primary reaction in each of these cases is undoubtedly one of solvolysis. The fractional distillation of the solvates 3ZrCl₄·2POCl₃ and 3HfCl₄·2POCl₃ appears to offer a promising method for the separation of zirconium and hafnium (48). The only solvate which has been reported for a group V halide is SbCl₅·POCl₃ (41).

A number of solvates of metal oxides have been prepared (49). The oxychloride reacts slowly at room temperature, but rapidly at 110°C., with calcium, magnesium, manganese(II), and zinc oxides to give solutions which, on cooling, deposit crystals of CaO·2POCl₃, MgO·

2POCl_3 or $\text{MgO} \cdot 3\text{POCl}_3$, $\text{MnO} \cdot 3\text{POCl}_3$, and $\text{ZnO} \cdot 3\text{POCl}_3$, respectively. With a number of other oxides, for example, Al_2O_3 , Cu_2O , CuO , HgO , Fe_2O_3 , and CoO , the reaction is more complex and deposits of metal chloride are formed. Treatment of calcium and magnesium hydroxides with phosphorus(V) oxychloride yields the disolvates (50). Hydroxides less ionic in nature appear to undergo solvolysis.

A series of electrolyses have been carried out in phosphorus(V) oxychloride (39). Attempts to reduce hexapositional chromium at the cathode when copper(II) chromate was employed as electrolyte were unsuccessful. The electrolysis of solutions of potassium iodate results in the deposition of potassium at the cathode and the formation of an anode product which gives tests for both chloride and phosphate ions. In addition, iodine is produced in solution. Upon electrolysis of iron(III) chloride, a thin, black, adherent deposit possessing strong reducing properties is formed at the cathode, and ferrous ion is obtained in solution.

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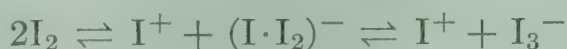
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HALOGENS AND INTERHALOGENS AS SOLVENTS *

Experimental work by Emeléus and his associates has shown in a most remarkable way how certain fundamental concepts can be applied to unusual solvents to lead the way to the preparation and characterization of completely new classes of compounds. Bromine trifluoride is hardly a solvent of general utility compared with those which have already been discussed. On the other hand, it is doubtful if many of the fluometallates could have been synthesized had it not been for the vision and imagination of Emeléus and his colleagues in undertaking a fundamental investigation of the solvent characteristics of bromine trifluoride and a number of related interhalogen compounds. The present work on the interhalogens as solvents supplements the earlier experimental studies of Jander and co-workers on liquid iodine as a solvent. Physical properties of iodine and a number of interhalogens are summarized in Table 78.

Liquid iodine (1) readily dissolves the alkali iodides and a few other metallic and non-metallic elements and compounds. (See Tables 80 and 81.) Quantitative values are available only for potassium iodide, which dissolves to the extent of 22 mole per cent at 113°C. with an increase to 24 mole per cent at 184°C. The influence of cation size upon the solubility of various compounds is evident both in liquid iodine and in other interhalogen solvents.

The conductivity of liquid iodine has been attributed to its auto-ionization in accordance with the following equilibria:



From these equilibria, it is to be anticipated that all soluble iodides will behave as bases, whereas substances such as iodine monochloride

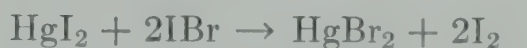
* The summary presented in this chapter is based upon an abstract of a paper presented by Mr. Niels C. Nielsen before the Inorganic Seminar at the University of Illinois, October 9, 1951. The authors take pleasure in acknowledging their indebtedness to Mr. Nielsen for permission to use this material.

TABLE 78

PHYSICAL PROPERTIES OF HALOGENS AND INTERHALOGENS

Property	I ₂	IF ₅	ICl	IBr	BrF ₃
Reference	(1)	(2)	(2)	(2)	(2)
Melting point, °C.	113.6	9.6	27.2 (α) 13.9 (β)	42	8.8
Boiling point, °C.	184.35	98	97-100	~116	127.6
Density, g./cc.	3.918 (at 135.5°C.)	3.33 (at 9.6°C.)	3.13 (at 45°C.)	3.7616 (at 42°C.)	2.843 (at 8.8°C.)
Specific conductivity, ohm ⁻¹ cm ⁻¹	1.7×10^{-4} (at 140°C.)	1.6×10^{-5} (at 9.6°C.)	4.42×10^{-3} (at 27.2°C.)	4.0×10^{-4} (at 42°C.)	8.1×10^{-3} (at 8.8°C.)
Viscosity, centipoises	1.414 (at b.p.)		4.19 (at 28.4°C.)		
Trouton constant	32.6	27.2	26.7		25
Dielectric constant	12.98 (at 168°C.)				

and iodine monobromide will behave as acids in this solvent. Evidence for such behavior has been found by conductivity measurements and neutralization reactions. The conductivity of a 4 mole per cent solution of rubidium iodide and of potassium iodide in liquid iodine is equivalent to the conductivity of a 2 mole per cent solution of potassium chloride in water. All the alkali metal iodides except those of sodium (and possibly lithium) act as strong electrolytes. Neutralization reactions have been shown to take place by conductometric and potentiometric titrations and by isolation of the salts which form.



Attention has been directed to examples of amphoterism, solvolysis, and solvation which take place in liquid iodine.

Only a small amount of information is available with respect to iodine pentafluoride as a solvent (3, 4, 5). Among the compounds known to be soluble in this medium are: SbF_5 , BF_3 , SO_3 , KIO_3 , AsF_3 , BrF_3 , and HF . Its conductivity may be due to self-ionization in accordance with the following equilibrium:



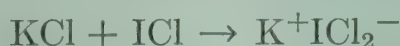
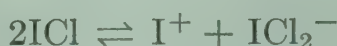
A one hundredfold increase in conductivity results when antimony pentafluoride is added to this solvent. Subsequent addition of potassium fluoride produces a typical neutralization reaction:



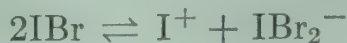
Solvolysis appears to occur quite readily in iodine pentafluoride and has prevented more careful study of this system.

As might be anticipated, iodine monochloride (6, 7, 8, 9) and iodine monobromide (10, 11) have similar solvent properties; iodine monobromide is the poorer solvent. Both compounds, especially iodine monochloride, will readily dissolve a large number of elements and also compounds which may be classified as acids and bases. (See Tables 80 and 81.) The chlorides and bromides of the heavier alkali metals are basic ansolvdes whereas the corresponding tin, antimony, and phosphorus halides may behave as acid ansolvdes. The following reactions illustrate (a) the self-ionization of these solvents and (b) typical reactions in the two systems:

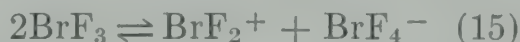
ICl



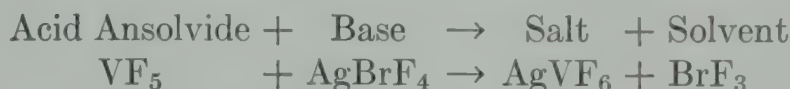
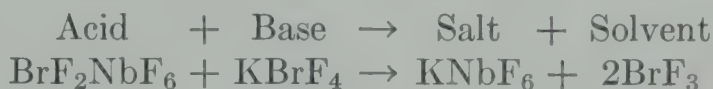
IBr



Numerous studies of the solvent properties of bromine trifluoride have demonstrated its usefulness in the preparation of unusual compounds and in the investigation of their physical and chemical properties. Considering its solvent properties with respect to fluorides, it appears to be somewhat less effective than iodine is toward iodides. However, because of its reactivity, bromine trifluoride serves as a solvent for a much wider range of substances which are first converted to fluorides before dissolving (12, 13, 14). (See Tables 79 and 81.) It presumably undergoes self-ionization as follows:



Basic and acidic ansolvides are well known in this system and follow the general pattern of the other interhalogen solvents. Neutralization reactions are represented by the following equations:



Solvolysis takes place readily in bromine trifluoride and, in many cases, has prevented the isolation of pure products (16). Reversibility has been shown to occur in the system



as verified by incomplete combination of the starting materials, by x-ray analysis indicating the presence of BrF_4^- ion in the product isolated, and by noting the occurrence of partial decomposition when a pure sample of potassium hexafluotitanate is treated with bromine trifluoride. Displacement reactions also take place, but more favorable compound formation has been obtained through neutralization reactions (17).

Initial study of the bromine trifluoride system led to the preparation and characterization of potassium, silver, and barium tetrafluorobromides (15). Many other complex fluorides, whose thermal instability negates their formation in good yield by using other procedures, have been prepared in bromine trifluoride, using metals, oxides, oxy

salts, and halides. Potassium, silver, and barium hexafluovanadates and the alkali salts of the hexafluotantalate, hexafluoniobate, hexafluobismuthate, and hexafluoroarsenate ions have all been made in bromine trifluoride (18, 19, 20, 21). Other reactions in this solvent led to the initial preparation of gold trifluoride (22). The simple fluorides of many metals are formed in bromine trifluoride (23, 24). The reactions of numerous oxides have been investigated; the results are summarized in Table 79 (12).

TABLE 79

BEHAVIOR OF OXIDES IN BROMINE TRIFLUORIDE

<i>Oxide</i>	<i>Compound Formed</i>	<i>% Yield</i>
BeO	BeF ₂	20
MgO	MgF ₂	25-30
HgO	HgF ₂	7
ZnO	ZnF ₂	23
CdO	CdF ₂	30
B ₂ O ₃	BF ₃	100
Al ₂ O ₃	AlF ₃	7
Tl ₂ O ₃	TlF ₃	100
PbO ₂	PbF ₄	70-90
SnO ₂	SnF ₄	20
ZrO ₂	ZrF ₄	13
Sb ₂ O ₃	SbBrF ₈	100
As ₂ O ₃	AsF ₅	100
Bi ₂ O ₃	BiF ₃	41-87
SeO ₂	SeF ₆	100
I ₂ O ₅	IF ₅	100
MoO ₃	MoF ₆	100

Among the many unusual reactions in bromine trifluoride are those involving the preparation of nitrosyl and nitronium complex fluorides and various fluosulfonates. A schematic presentation of such reactions is given in Figure 31.

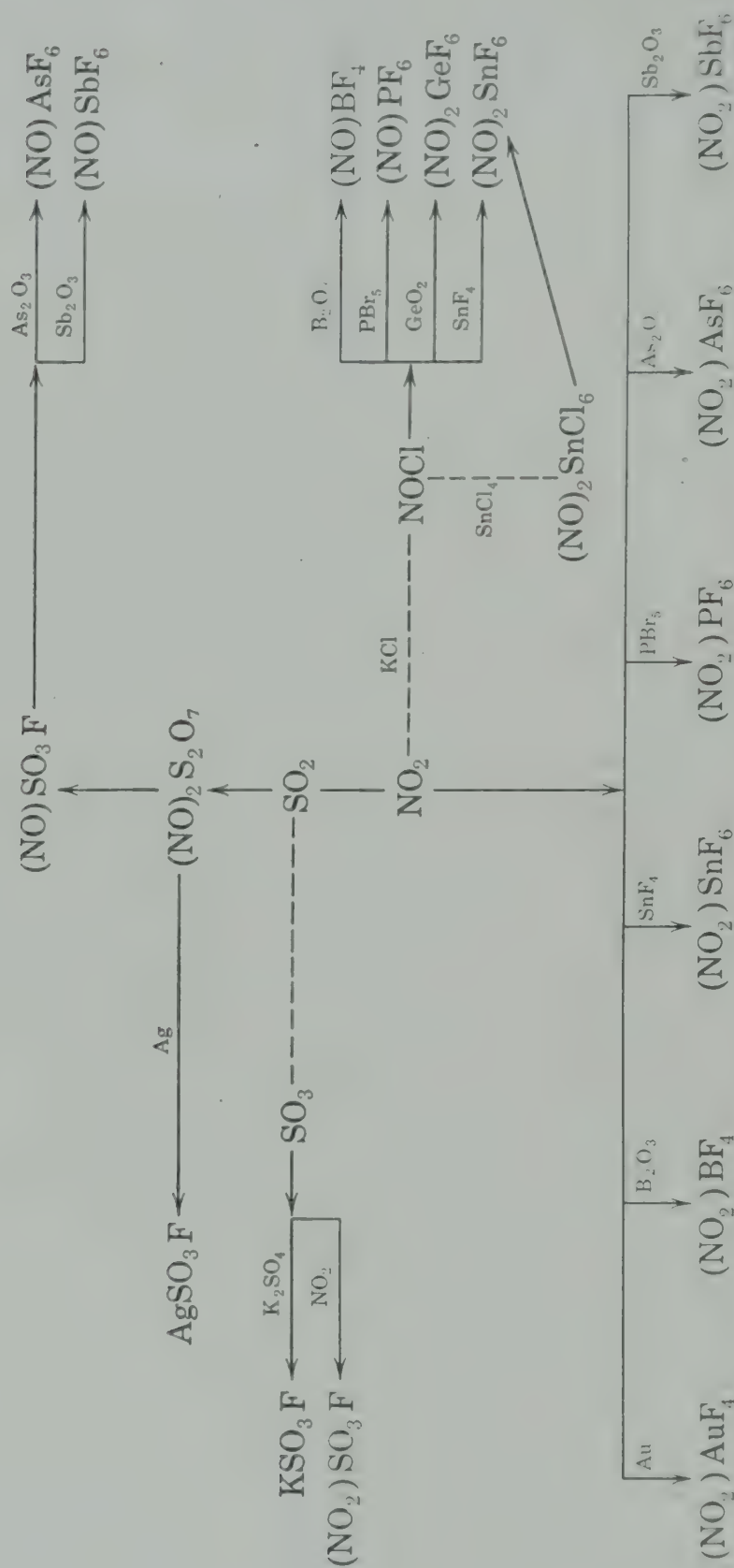


FIGURE 31. Preparation of nitrosyl and nitronium complex fluorides and fluosulfonates in bromine trifluoride (17). Solid lines indicate reactions taking place in bromine trifluoride; dotted lines indicate intermediate reactions.

TABLE 80
BEHAVIOR OF ELEMENTS IN VARIOUS SOLVENTS
Solubility or Compound Formed * in

<i>Element</i>	<i>I₂</i>	<i>ICl</i>	<i>IBr</i>
Na		NaCl	NaBr
K		<i>KICl₂</i>	<i>KBr—KIBr₂</i>
Cu	Insoluble	CuCl ₂	<i>CuBr₂</i>
Ag	Insoluble	<i>AgCl</i>	AgBr
Au		<i>AuCl₃</i>	<i>AuBr₃</i>
Mg	Insoluble	MgCl ₂	MgBr ₂
Ca		CaCl ₂	CaBr ₂
Ba		<i>BaCl₂</i>	BaBr ₂
Zn	Insoluble	<i>ZnCl₂</i>	ZnBr ₂
Cd	Insoluble	Insoluble	Insoluble
Hg		<i>HgCl₂</i>	<i>HgBr₂</i>
B		Insoluble	Insoluble
Al	AlI ₃	<i>AlCl₃</i>	<i>AlBr₃(?)</i>
In		InCl ₃ (?)	(Surface reaction)
Ti		<i>TiCl₄</i>	<i>TiBr₄(?)</i>
Zr		Insoluble	Insoluble
C		Insoluble	Insoluble
Si		Insoluble	Insoluble
Ge		<i>GeCl₄(?)</i>	<i>GeBr₄(?)</i>
Sn	SnI ₄	<i>SnCl₄</i>	<i>SnBr₄</i>
Pb	Insoluble	Insoluble	Insoluble
V		<i>VCl₃</i>	<i>VBr₃</i>
Nb		Insoluble	Insoluble
Ta		Insoluble	Insoluble
P		<i>PCl₅</i>	<i>PBr₅—PBr₅·IBr</i>
As	AsI ₃	<i>AsCl₃</i>	<i>AsBr₃(?)</i>
Sb	SbI ₃	<i>SbCl₅</i>	<i>SbBr₃</i>
Bi	BiI ₃	<i>BiCl₃</i>	<i>BiBr₃</i>
Cr	Insoluble	Insoluble	Insoluble
Mo		Insoluble	Insoluble
W		Insoluble	Insoluble
S	Soluble	<i>S₂Cl₂(?)</i>	<i>S₂Br₂(?)</i>
Se	Soluble	<i>SeCl₄(?)</i>	<i>SeBr₄(?)</i>
Te	Soluble	<i>TeCl₄</i>	<i>TeBr₄</i>
Mn		MnCl ₂	MnBr ₂
Fe	FeI ₃	<i>FeCl₂, FeCl₃</i>	<i>FeBr₃</i>
Co		CoCl ₂	CoBr ₂
Ni	Insoluble	NiCl ₂	NiBr ₂
Pt	Insoluble	Insoluble	Insoluble

* Italicized compounds are formed in yields equal to or greater than 50%.

TABLE 81

SOLUBILITY OF HALIDES IN VARIOUS SOLVENTS

<i>Cation</i>	<i>Iodide in I₂</i>	<i>Chloride in ICl</i>	<i>Bromide in IBr</i>	<i>Fluoride in BrF₃</i>
Li ⁺	Soluble	Slightly sol.	Very sl. sol.	Slightly sol.
Na ⁺	Soluble	Slightly sol.	Very sl. sol.	Soluble
K ⁺	Soluble	Very soluble	Very soluble *	Soluble
Rb ⁺	Soluble	Very soluble	Very soluble	Soluble
Cs ⁺	Soluble	Very soluble.	Very soluble	Soluble
NH ₄ ⁺	Soluble	Very soluble	Very soluble.	
Cu ⁺²				Insoluble
Ag ⁺		Insoluble		Soluble
Ag ⁺²				Insoluble
Au ⁺³				Soluble
Be ⁺²	Insoluble			Insoluble
Mg ⁺²	Insoluble			Insoluble
Ca ⁺²	Insoluble			Very sl. sol.
Sr ⁺²	Insoluble	Insoluble	Mod. soluble	
Ba ⁺²	Insoluble	Insoluble	Mod. soluble	
Zn ⁺²			Mod. soluble	Insoluble
Cd ⁺²				Insoluble
Hg ⁺²	Soluble			Insoluble
B ⁺³				Soluble
Al ⁺³	Soluble	Soluble	Mod. soluble	Insoluble
Ga ⁺³				Insoluble
In ⁺³				Insoluble
Tl ⁺	Soluble			
Tl ⁺³				Insoluble
Ti ⁺⁴		Mod. soluble		Soluble
Zr ⁺⁴				Insoluble
Ce ⁺³				Insoluble
Ce ⁺⁴				Soluble
Th ⁺⁴				Insoluble
Si ⁺⁴		Soluble		Soluble
Ge ⁺⁴				Soluble
Sn ⁺⁴	Soluble	Soluble	Very sl. sol.	
Pb ⁺²	Soluble(?)			Insoluble
Pb ⁺⁴				Insoluble
V ⁺⁴		Soluble		
V ⁺⁵				Soluble
Nb ⁺⁵		Soluble	Insoluble	Soluble
Ta ⁺⁵			Insoluble	Soluble
P ⁺³	Soluble	Soluble	Very soluble	
P ⁺⁵		Soluble	Very soluble	Soluble
As ⁺³	Soluble			
As ⁺⁵				Soluble

* KI is also very soluble.

TABLE 81 (*Continued*)

SOLUBILITY OF HALIDES IN VARIOUS SOLVENTS

Cation	Iodide in I_2	Chloride in ICl	Bromide in IBr	Fluoride in BrF_3
Sb^{+3}	Soluble		Mod. soluble	
Sb^{+5}		Slightly sol.		Soluble
Bi^{+3}	Soluble			Insoluble
Bi^{+5}				Soluble
Cr^{+3}				Insoluble
Mo^{+2}			Mod. soluble	
W^{+2}			Mod. soluble	
SO^{+2}		Soluble †	Insoluble	
Mn^{+2}				Insoluble
Mn^{+3}				Insoluble
Fe^{+3}	Soluble			Insoluble
Co^{+2}				Insoluble
Co^{+3}				Insoluble
Ni^{+2}			Insoluble	Insoluble

† Miscible in all proportions.

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HIGH-TEMPERATURE SYSTEMS *

Present-day knowledge concerning solvents and relationships in solvent-solute systems is based largely upon behavior and observations over a rather limited temperature range. Up until fifty years ago little or no effort was made to carry out reactions in solvents at temperatures below 0°C. Study of reactions in liquid ammonia and in liquid sulfur dioxide did make it necessary for the investigator to consider the use of solvents which are liquid at ordinary pressures only at temperatures considerably below room temperature. Reactions at higher temperatures, however, rarely exceeded the boiling point of the solvent (or solution), even though the development of high-pressure techniques did extend this range somewhat. It is significant, however, that many of the more important technical processes in the fields of metallurgy and ceramics, some of which date back centuries, involve liquid phase high-temperature reactions. A study of geochemical phenomena has likewise led to the conclusion that many of the processes resulting in formation of minerals and ore deposits in nature must have taken place at temperatures far above the range in which we are accustomed to work.

Information concerning high-temperature reactions is not so readily available, nor have the data been so well organized as they have been for systems which are employed at ordinary temperatures. However, a survey of important metallurgical and ceramic processes reveals that all the types of reactions which are recognized as being capable of taking place in solvent-solute systems at ordinary temperatures also occur at higher temperatures in fused melts. Binary and multicomponent systems have been studied extensively in connection with production of glasses and of slags. Fused melts are employed as high-temperature electrolytes for the production of metals, particularly those which cannot be electrodeposited from aqueous and non-aqueous

* The subject matter in this chapter represents an adaptation and extension of the material presented by L. F. Audrieth in the Priestley Lectures, given at the Pennsylvania State College in April, 1949 (1).

solutions at room temperature. Although reaction occurs in many instances between the components of such high-temperature systems with formation of definite compounds, there are some unusual cases of outright solubility which deserve more than passing comment. Fused alkali fluorides and chlorides have long been used as solvents for metallic oxides; the solutes appear to depolymerize and exist as ionic species in such melts. Barites for the production of high-grade "blanc fixe" can be purified by solution of the crude product in fused sodium chloride; the silica and iron impurities are insoluble (2). Reaction takes place between barium sulfate and sodium carbonate, both of which are soluble in fused sodium chloride, to form the less soluble alkaline earth carbonate. A process embodying the use of fused sodium chloride as a solvent for this purpose is claimed to have definite advantages over the older method in which the sulfate is reduced to the sulfide and then converted to the carbonate by metathesis in aqueous solution.

Examples of limited miscibility and phenomena of phase separation are common in many metallurgical procedures where metal and slag separate as immiscible phases. The Orford process for purification of nickel matte depends upon the fact that molten nickel sulfide separates as an immiscible phase from a sodium sulfide layer which extracts (or reacts) with the iron and copper sulfide contaminants. The colloidal nature of tin(IV) oxide, titania, zirconia, and tricalcium phosphate, which are used as opacifiers in enamels, and of elemental gold and selenium, which find application as colorants in glasses, has been established for various silicate systems in which these agents are incorporated.

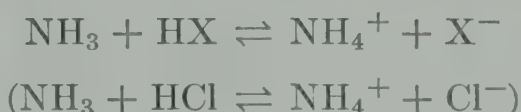
Chemical and electrochemical oxidation-reduction reactions could also be cited, but to cover all possible reactions and phenomena in fused systems is beyond the scope of this book. Rather than to attempt to discuss in general terms the use of fused melts as media for chemical reactions, it is proposed specifically to show how those acid-base relationships which define behavior in solvent systems at ordinary temperatures can be extended to high-temperature anisolvous media. Those substances which ceramists and metallurgists have conventionally designated as acidic and basic fluxes since the days of Berzelius may indeed be considered acids and bases, respectively, by extension of the protonic theory and the more generalized electronic concept. Many reactions of polymerization and depolymerization in oxide systems are brought about by appropriate changes in the acidic or basic nature of such melts. It is even possible to generalize still further within the realms of concepts proposed by Fajans and to consider acid-base relationships, in so far as they affect the fundamental nature of

such systems, as manifestations of the polarizing (deforming) effect of particles of varying formal positive charge and size upon the more readily deformable negative components.

PROTONIC ACIDS AT HIGHER TEMPERATURES

According to the protonic concept (Brönsted-Lowry) any molecule or ion which is a potential proton donor may be regarded as an acid. Such acids undergo reaction with the solvent to increase markedly the concentration of the "onium" ion (the solvated proton), which represents the actual bearer of acidity in each medium—the hydronium ion in water, the ammonium ion in ammonia, and the substituted ammonium ion in the corresponding amine, etc. The solvent system concept also leads to this same conclusion—ammonium salts dissolved in liquid ammonia represent acidic solutions; amine salts greatly increase by solution in the parent amine the concentration of the onium ion derivable by self-ionization of the solvent. Despite the fact that these compounds are designated as salts, they yield acidic solutions in their respective parent solvents since they contain ions which under proper circumstances release the proton.

It is also recognized that many ammonium salts undergo dissociation at higher temperatures to form ammonia and the corresponding hydrogen compounds. This is the reverse of the reaction which occurs when the corresponding hydrogen compounds are dissolved in liquid ammonia, or react with ammonia in aqueous solution or in some non-aqueous solvent:

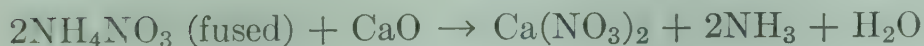


The onium ion is thus capable of releasing the proton at higher temperatures. By all criteria which apply in solvent systems at ordinary temperatures, the onium ion per se is a stronger acid under these conditions than it is in a solvent medium. In fact, it seems reasonable to state that the chloride ion is a stronger base at higher temperatures than the ammonia molecule!

Countless examples of chemical reactions involving onium salts can be gleaned from the literature to show that these substances do indeed act as acids in the solid as well as in the fused states at higher temperatures. Even though interionic attraction is greater in these very concentrated "solutions" which are obtained upon fusion, the presence of the onium ion should impart acidic character to such melts. Such

substances as ammonium sulfate and ammonium fluoride have long been used for the opening up of complex ore minerals. There are many examples of reactions of metals, oxides, and carbonates with ammonium salts at higher temperatures. So far as the end products are concerned, such reactions resemble those which take place in aqueous or liquid ammonia solutions of the acids. Anhydrous chlorides can be prepared by heating the hydrated chlorides in the presence of ammonium chloride, which serves to repress hydrolysis and the formation of basic salts, presumably because such dehydration is taking place in an acid medium. A more complete discussion of reactions in several typical fused onium salts very definitely leads to the conclusion that these actually behave as acids at higher temperatures.

REACTIONS IN FUSED AMMONIUM NITRATE (3). Ammonium nitrate is stable at its melting point and is a good conductor of the electric current. Fused ammonium nitrate represents, in effect, a very concentrated (equimolar) solution of nitric acid in liquid ammonia. The positions of the ammonium and nitrate ions are fixed in the crystal lattice in the solid state. In the fused state, however, these ions possess appreciable mobility, even though restricted because of interionic attraction between the positively and negatively charged particles. The oxides of copper(II), uranium(VI), magnesium, cadmium, lead(II), calcium, nickel, mercury, barium, and zinc dissolve in fused ammonium nitrate, with the formation of the metallic nitrates, ammonia, and water. From the older classical viewpoint as extended by the solvent system concept, these reactions are intermediate between an aquo neutralization and an ammono neutralization:



It is well known that nitric acid is incapable of dissolving certain oxides. In like fashion no reaction is observed between fused ammonium nitrate and the oxides of beryllium, aluminum, chromium(III), iron(III), thorium, tin(IV), and the more "acidic" oxides of tantalum, niobium, vanadium, molybdenum, and tungsten. It is interesting, however, in this connection to point out that the hydrated nitrates of thorium, beryllium, and aluminum are soluble in fused ammonium nitrate, even though the corresponding oxides do not appear to react. The carbonates of the alkaline earth metals and manganese(II) also react with fused ammonium nitrate to yield the corresponding nitrates.

Metallic zinc, cadmium, magnesium, cobalt, nickel, copper, and bismuth react vigorously (Caution! Danger!) with the fused nitrate and are taken into solution with evolution of nitrogen and ammonia. The reaction with copper can be represented essentially by the following equation:



A fused melt containing a small amount of ammonium chloride dissolves gold. Sulfides of zinc and lead are attacked slowly to yield mixtures of the corresponding nitrates and sulfates. Copper(I) oxide is oxidized to the copper(II) state, iron(II) chloride to iron(III) oxide, tin(II) chloride to tin(IV) oxide, and hydrated chromium(III) nitrate to the dichromate. The last reaction is especially interesting since the hydrated chromium(III) nitrate dissolves to give a green melt which rapidly changes to the yellow-orange color of the dichromate. Complete oxidation takes place readily.

AMMONIUM CHLORIDE (4, 5, 6). It is not necessary to effect fusion of an onium salt in order to take advantage of the acidic character of such compounds. Ammonium chloride will react rapidly at 250°C. with rare earth oxides, and oxides of iron(III), lead(II, IV), manganese(IV), antimony(III), cadmium, and magnesium to yield the corresponding chlorides. Indefinite products are obtained from oxides of nickel, copper, and vanadium. Zinc oxide reacts to give a mixture which, after removal of the excess ammonium chloride, yields a product that may be distilled unchanged at red heat and is presumably the compound $\text{ZnCl}_2 \cdot \text{NH}_3$. Anhydrous rare earth chlorides may be prepared by mixing the rare earth oxides with an excess of ammonium chloride, heating at about 200°C. to effect conversion into the chloride, and then removing the excess ammonium chloride by sublimation under reduced pressure at 300 to 350°C. (7).

In contact with air and at temperatures between 200 and 300°C. ammonium chloride rapidly corrodes most of the common metals, such as iron, nickel, copper, tin, and magnesium, and alloys, such as brass, bronze, Monel metal, Inconel, Hastelloy A, C, and D, and high- and low-carbon steels. Nickel seems to stand up best in a vacuum. It is significant in this connection that ammonium chloride vapor is more active than dry hydrogen chloride.

Ammonium chloride forms quite a number of double salts. Many of these products are stable at their melting points and constitute distinctly acidic melts in the fused state. Zinc ammonium chloride, which is a typical example of such a double salt, is widely used as a galvanizing flux. It is probable, however, that this compound is actually an

ammonium chlorozincate, since its efficiency as a metal cleaner decreases as the ammonia content is reduced.

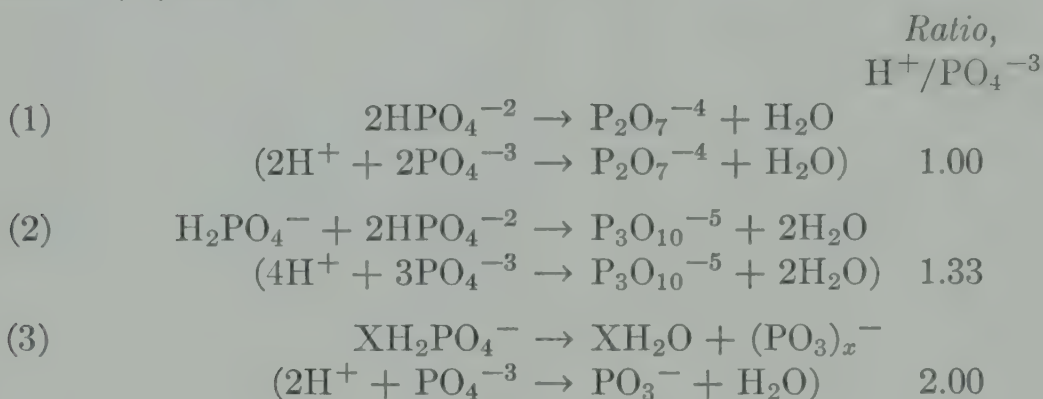
MISCELLANEOUS ONIUM SALTS. Pyridine hydrochloride (8) melts at $144.5^{\circ}\text{C}.$, and in the molten state reacts rapidly with aluminum, cadmium, calcium, magnesium, zinc, and even copper to form hydrogen and the corresponding chlorides which are soluble in the melt. Manganese, nickel, tin, lead, and iron react in the same fashion but less rapidly. Oxides of antimony(III), barium, bismuth(III), cadmium, cobalt(II), copper(I, II), iron(III), mercury(II), lead(II), magnesium, manganese(IV), and nickel(II) also dissolve readily. Electrolysis of melts prepared either by solution of the metal, of the oxide, or of the chloride in fused pyridine hydrochloride yields metallic deposits in the case of antimony, arsenic, bismuth, lead, mercury, and tin.

Similar observations have also been found to hold qualitatively for other onium salts such as those obtained from such nitrogen bases as hydrazine, hydroxylamine, aniline, phenylhydrazine, and various simple amines (9). Ammonium thiocyanate and ammonium acetate may be cited as further examples of useful fused ammonium salts in addition to the sulfate and the fluoride which were mentioned earlier. These experimental findings may be cited as qualitative evidence for the contention that the characterization of onium salts as acids per se in the solid and fused states is one of the most useful extensions of the protonic theory (9).

ANIONIC ACIDS. The literature offers much experimental evidence to demonstrate that salts consisting of a metallic ion and a hydrogen containing anion may also act as acids per se at higher temperatures and in the fused state. One of the most useful of these "salts which are acids" is potassium hydrogen fluoride, KHF_2 , which is employed to effect solution of ore minerals containing silica, titania, and other refractory oxides such as those of niobium and tantalum. Potassium hydrogen sulfate is used to decompose ores of titanium and zirconium, and siliceous rare earth minerals. Fusion with sodium hydrogen sulfate brings about solubilization of carnotite. The alkali mono- and dihydrogen phosphates are extremely corrosive materials at higher temperatures as indicated by their ability to attack many of the common metals. All these substances are typical acidic fluxes; from the more modern point of view they are acids since they contain anions which are proton donors.

Reactions involving "molecular dehydration" of the mono- and dihydrogen phosphates at higher temperatures may be regarded as examples of polyanionic aggregation, the extent of such aggregation

being dependent upon the potential acid character of the starting materials and the temperature (10). Thermal methods for the preparation of the poly- and metaphosphates are usually represented by equations 1, 2, and 3:



$$X = 3 \text{ or } X$$

Since these equations do not, however, reveal their true nature as acid-base reactions they have been represented (in parentheses) as reactions involving increasingly greater aggregation as the potentially available proton concentration is increased. The hydrogen ion:phosphate ion ratio is given in each instance. These reactions are therefore similar to the better-known examples of polyanionic aggregation which chromates, tungstates, molybdates, and vanadates undergo as the hydrogen ion concentration is increased, but differ in that condensation polymerization of the phosphate ion does not take place in aqueous solution. Structurally, conversion of the orthophosphates into poly- and metaphosphates may be regarded as the joining together of phosphate tetrahedra by removal of oxide ions to form either chain or cyclic structures. The polyanionic species which are thus formed become increasingly more acidic in character as their composition approaches that of phosphorus(V) oxide. (See also p. 268 for discussion of the metaphosphate ion as an acid.)

THE ELECTRONIC THEORY AS APPLIED TO ACID-BASE REACTIONS AT HIGHER TEMPERATURES (11)

There are many high-temperature reactions which are not amenable to treatment in terms of the protonic concept because of the complete absence of any hydrogen-containing ion. It is in these instances that the electronic (Lewis) concept may be applied with particular advantage since a base is defined as an electron pair donor and an acid as an electron pair acceptor. Many of the high-temperature reactions

between so-called basic oxides, sulfides, and fluorides and such acidic oxides as silica and titania, and acidic metaphosphate and metaborate melts, may be looked upon as typical acid-base reactions from this particular point of view. Although fusion takes place in many instances, a change in state is not always necessary. Many of the important high-temperature technical processes involve sintering reactions. Typical high-temperature acid-base reactions which are important in ceramic, metallurgical, and analytical processes are summarized in the Table 82.

TABLE 82

THE ELECTRONIC THEORY AND ACID-BASE REACTIONS AT HIGHER TEMPERATURES

Class	Bases	Acids	Neutralization Products	Applications
1	O^- (from MO, MOH, MCO_3 , MSO_4)	SiO_2 Al_2O_3 B_2O_3	SiO_3^{--} or SiO_4^{-4} AlO_2^- or AlO_3^{-3} BO_2^- or BO_3^{-3}	Manufacture of glass, cement, and ceramic products. Slag formation.
2	O^- (from MO)	BO_2^- (B_2O_3) PO_3^{--}	BO_3^{-3} PO_4^{-3}	Borax bead test. Metaphosphate bead test.
3	O^- (from MO, etc.)	$S_2O_7^{--}$ ($SO_4 \cdot SO_3^-$) HSO_4^- ($H_2O + S_2O_7^{--}$)	SO_4^{--}	Solubilization of ore minerals.
4	S^- (from Na_2S)	FeS Cu_2S	FeS_2^{--} CuS^-	Orford process for nickel concentration.
5	F^- (from alkali fluorides)	BeF_2 AlF_3 TaF_5	BeF_4^{--} AlF_6^{-3} TaF_7^{--}	Electrolytic melts.

The interrelationships listed in Table 82 must be considered as somewhat formal in nature. Empirical formulas are used to represent the compositions of the reactants. Many of the acidic oxides such as silica are represented as electron-deficient simple molecules but are actually giant molecules which very definitely undergo depolymerization before the ions listed in Table 82 are actually obtained if, indeed, they even exist. Thus, for instance, the chemical attack of silica by fusion with sodium hydroxide or other compounds yielding strong anion bases undoubtedly proceeds through the intermediate formation of polyanionic silicate complexes, the average ionic sizes of which must depend upon both the temperature and the quantity of added base. It is completely illogical to consider reactions of a highly polymerized

aggregate of this sort with some other substance as involving complete and immediate disruption of such a giant lattice. Just as the isopoly and heteropoly anions in aqueous solution can be degraded to the simple ions by raising the pH , so can the giant molecule of silica be degraded to simpler ionic species by the action of basic fluxing agents such as the metallic oxides, the hydroxides, or carbonates. Such depolymerization can also be effected by fluorides. Quite apart from the fact that the fluoride ion is an anion base, its inability to serve as a bridging group between two silicate tetrahedra makes it a very effective depolymerizing agent. This explanation would seem rational since fluorides are used technically to decrease the viscosities of silicate melts and slags. The sintering reactions which take place in the manufacture of cement also can be looked upon as high-temperature acid-base reactions where both alumina and silica function as acids.

The second group of reactions listed in Table 82 includes the bead tests formerly so much used in analytical chemistry. In each of these the anion of the low-melting fused salt functions as an acid in accepting an electron pair from the basic oxide ion. In these instances, however, it is the acid species which is a polymeric aggregate and which reacts with oxides to form intermediate polyanionic complexes. The polymetaphosphate ion undergoes depolymerization, with the formation of definite ionic aggregates such as the tri- and pyrophosphate as intermediates with the orthophosphate as the coordinatively saturated end product. Actually, the metallic ortho- and pyrophosphates have been identified as the reaction products in the metaphosphate bead test.

Although the metaborate bead test has normally been used for the characterization of oxides, it is interesting to note that cobalt is identified by means of a bead test upon the precipitated sulfide. Fluoroborates have been obtained by fusing boric oxide and the alkali fluorides. Furthermore, the fact that boric oxide decomposes nitrates, sulfates, and other oxy salts at elevated temperatures, with the production of metaborates and the displacement of the more volatile acids or their decomposition products, certainly agrees with the Lewis interpretation.

The well-known solubilizing effects of fusion with alkali hydrogen sulfate or pyrosulfate, especially in the treatment of such refractory ores as those of titanium, tantalum, and niobium, may also be interpreted as acid-base reactions at higher temperatures. Although reference has already been made to these reactions in connection with the discussion of the protonic anion acid, the HSO_4^- ion, it must also be

borne in mind that thermal dehydration occurs with formation of the pyrosulfate ion. The pyrosulfate ion may be regarded either as a polyanionic Lewis acid, similar to the metaphosphate, or as a source of sulfur trioxide, which in the monomolecular state is a coordinatively unsaturated molecular acid.

In such melts as are furnished by molten sodium sulfide, the sulfide ion is a strong base. Thio complexes are common, and their formation in the molten state is accomplished in an interesting series of metallurgical processes, for instance, in the refining of nickel where the copper(I) and iron(II) sulfides dissolve in fused sodium sulfide and are thus separated from the nickel sulfide, which undergoes little or no reaction. Molten mixtures of sodium and copper(I) sulfides show electrolytic conduction; the existence of a CuS^- ion has been demonstrated. The formation of sodium monothioorthophosphate, $\text{Na}_3\text{PO}_3\text{S}$, by fusion of equimolecular quantities of sodium sulfide and sodium metaphosphate is cited as an additional example in which the strong anion base, the sulfide ion, effects depolymerization of the acidic poly-metaphosphate ion.

Many metallic fluorides and oxides dissolve in an excess of molten alkali fluoride to form complex ions, the fluoride ion acting as a strong base in bringing about these reactions. The small radius of the fluoride ion undoubtedly contributes to the formation of extremely stable complexes of relatively low ionic weights which yield melts of high fluidity and excellent conductivity. Reference has already been made to the depolymerizing action of the fluoride ion on silicate melts. This same behavior is also encountered in the polymetaphosphate system. Study of this reaction has led to the development of a simplified procedure for preparation of alkali monofluophosphates by fusion of the respective fluoride with the metaphosphate (10). Fluorides have long been recognized as mineralizers when found with certain classes of ore deposits. Fluorspar, together with other fluoride-containing minerals, is found in the end fractions of magmatic intrusions as well as in the surrounding and sometimes highly metamorphosed country rock.

The opening up of ores in general necessitates the use of a wide variety of fluxes, the choice of flux in each instance being governed by a knowledge of the chemical composition of the ore mineral. For acidic ores the high-temperature bases such as sodium hydroxide, carbonate, or fluoride, calcium carbonate or oxide, and potassium fluoride are widely used, whereas for basic ores such acidic fluxes as silica, borax, bisulfate, or pyrosulfate are important.

ACID-BASE RELATIONSHIPS IN OXIDE SYSTEMS

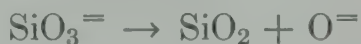
There is no question but that oxide systems are the most important high-temperature systems encountered in practice. The acidic and basic properties of various oxides are characterized by their ability to react mutually, usually at higher temperatures, to form compounds which may be considered as neutralization products:



With these facts in mind, a more precise acid-base definition applicable specifically to oxide systems has been proposed by Lux (12). This relationship can be represented by the type equation:

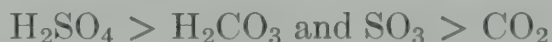


and can be illustrated by the following examples:



There is a distinct analogy between acid-base functions of such oxide systems and those which characterize protonic systems in which acids represent potential proton donors. The Lux proposal defines bases as oxide ion donors. Acid-base relationships in such oxide systems involve the transfer of the oxide ion from one state of polarization to another state in which it is more highly polarized.

The Lux concept has been further advanced by Flood and Förland (13), who point out that there is at least a "qualitative parallelism between proton affinity and the tendency to split off an oxygen ion as will be seen in comparing acid strength of the compounds:



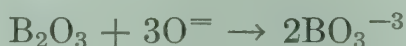
"The stronger bond between the oxygen and the central atom is in turn usually connected with a weaker binding tendency for a proton to that oxygen atom." These same authors point out that the systems which are considered in such oxide melts are built up of large oxygen ions and relatively small cations. Such oxygen ions are, therefore, always more or less polarized (deformed) by the adjacent cations. The situation in such non-solvent systems is quite different from that which characterizes use of solvents for the reason that the mutual

interaction of particles of opposite charge is a more important consideration than in the more familiar instances where charged particles (ions) are solvated and separated by solvent sheaths. Three important types of acid-base transitions are met in such oxide systems:

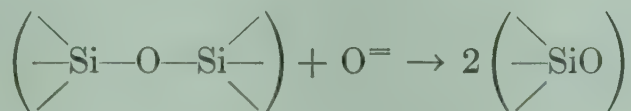
A. Atoms with high ionization energy such as sulfur and carbon frequently give acid-base transitions accompanied by an alteration of their coordination number for oxygen:



B. For atoms with medium ionization energy the coordination number may remain unchanged:

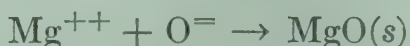


In these instances, the acid-base transition consists in the breaking of an oxygen bridge between two connected structural units such as characterize the tetrahedral silicate groups:



It is specifically emphasized, therefore, that the transition of an acid to a corresponding base is connected with a breakdown in the macromolecular structure of such aggregates.

C. For atoms with low ionization energy, which easily form cations, the acid-base transition may be connected with the formation of an oxide phase:



Of particular interest are those cases where the acid-base transitions in oxide systems bring about the depolymerization reactions to which reference has already been made in connection with an exposition of the electronic concept as applied to high-temperature reactions. This is particularly true of the so-called polyacids in which the linking of simple structural units to form large complexes can be represented by formation of oxygen bridges of the type X-O-X. This situation holds not only in silicate systems in which silicate tetrahedra are joined together by oxygen atoms which are shared mutually to form two-and-three dimensional structures, chains, and rings, but applies

also to other isopolyacid systems such as the polyphosphates, polymetaphosphates, and even the polyacids of chromium and sulfur, in each of which a tetrahedral XO_4 unit is prescribed. Similar considerations probably also apply to the polymolybdates and the polytungstates in which the central atoms are hexacovalent, and in each of which the structural unit is probably octahedral.

The transition of a polyacid to the corresponding base (the product of lower ionic-molecular weight) thus consists in the breaking of oxygen bridges and the simultaneous acceptance of an oxygen ion from some oxygen ion donor material that may be regarded as a base. The acid-base reaction is thus connected with the disintegration of the molecular structure, that is, with a depolymerization of a poly complex to form simpler and smaller particles.

This concept of oxygen ion transfer, as applied fundamentally to acid-base relationships in such condensed systems, has a great deal of merit and is a very useful point of view. Although this particular approach is limited in its present form only to oxide systems, it is conceivably applicable also to sulfide systems in which the greater deformability of the sulfide ion must be taken into consideration. Fluorides, however, also depolymerize such condensed oxide systems. It is for this reason that the more general electronic concept, despite its shortcomings, is perhaps more widely applicable, since a variety of anionic bases effect similar depolymerizations (10).

In concluding this general discussion of acid-base relationships in high-temperature systems, it may be well to bring up another very important point which is often overlooked by those who ascribe acid or base character either to some one particular ionic species such as the proton or the oxide ion, or to some one particular process such as the coordination process which is inherent in the electronic theory. Limitation of acid-base phenomena only to those systems in which proton or oxide ion transfer takes place completely eliminates similar and analogous phenomena in which these ionic species are not present. There are many positive ions which in their reactions and properties do not differ too greatly from the proton. Recognized differences rest largely on the fact that the proton is the smallest positively charged particle and as such does possess an appreciable deforming effect upon negative ions. The polarizing tendency in bringing about deformation of negative ions is definitely a function of the size and formal charge of the positive constituent. Conversely, the tendency for a negative ion, be it the oxide, sulfide, or any other negatively charged particle, to suffer deformation depends upon its size and charge. These considerations are the basis for the concepts which Fajans has championed

so vigorously. The tendency for the bond between two particles of opposite charge to become more and more covalent in character is a function of charge and size of each. The higher the charge and the smaller the positive ion, the greater will be its deforming effect upon the negative particle. The larger the negative particle and the greater its charge, the greater will be the tendency for the resulting linkage to become covalent in character.

The conclusion is obvious; other positive ions besides the proton possess acid character. The smaller the positive particle and the higher its charge, the more reasonably can such a cation be looked upon as an acid analog. Proton-like character can, therefore, be ascribed to any positive ion.

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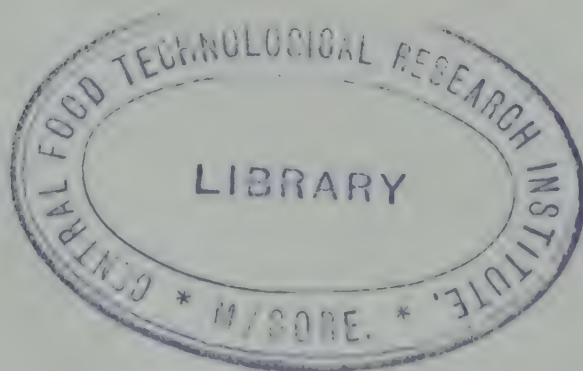
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